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Historically Accurate Reconstructions and Characterisation of *Chrome Yellow Pigments*

By

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Resumo

Um conhecimento detalhado dos materiais utilizados pelos artistas é fundamental para compreender as suas técnicas e contextualizar as suas obras, mas também para o estabelecimento das técnicas de conservação e restauro mais adequadas. Este conhecimento provém de fontes documentais fidedignas contendo informações técnicas contemporâneas aos artistas e da preparação de reproduções com rigor histórico. Decifrar as palavras do passado no sentido de desvendar tecnologias artísticas reveste-se de particular complexidade e constitui um dos campos mais desafiantes da área da conservação do património cultural.

O pigmento amarelo de crómio pertence à paleta artística do século XIX tendo sido entusiasticamente utilizado por diversos artistas, como por exemplo Amadeo de Souza-Cardozo, mesmo quando o seu uso era desaconselhado.

O objectivo principal deste trabalho foi a reprodução de pigmentos amarelo de crómio com o maior rigor histórico possível, recorrendo à base de dados *Winsor & Newton 19th Century Artists' Materials*, tendo sido pela primeira vez utilizada de um modo sistemático na reprodução de pigmentos. Consequentemente, as receitas retiradas da base de dados foram decompostas nos seus passos mais relevantes, tendo sido possível estabelecer uma correspondência correcta entre os materiais usados originalmente e os seus equivalentes actuais.

Um total de 34 pigmentos e 3 minerais foram caracterizados por EDXRF, Raman, FTIR, XRD e SEM-EDS tendo-se que o cromato de chumbo foi identificado na maioria das suas composições, independentemente da receita ou das variações dos processos. A detecção de outros compostos também foi possível consoante o valor de pH, ou seja, cromato básico de chumbo foi obtido em condições alcalinas, conferindo uma tonalidade alaranjada aos pigmentos, e cristais mistos de cromato e sulfato de chumbo formam-se em condições ácidas, apresentando uma tonalidade mais amarelada. Todos as cargas utilizadas foram identificadas, nomeadamente, a calcite, a barite e o gesso. Contudo, outros compostos também foram detectados, concretamente, cerussite e calcite, mesmo quando estes não foram adicionados durante a produção dos pigmentos.

Por fim, procedeu-se a uma comparação entre os pigmentos sintetizados e amostras de casos de estudo, onde foi possível identificar cromato de chumbo e cristais mistos de cromato e sulfato de chumbo na presença de calcite, barite e cerussite. Desta forma, estabeleceram-se propostas relativamente aos processos de produção dos pigmentos amarelo de crómio presentes nas amostras de casos de estudo.

A abordagem multi-analítica adoptada foi crucial para a caracterização de todos os pigmentos.

Abstract

A detailed knowledge of the materials used by artists is essential to unveil their techniques and to place their works in context as well as to establish the most adequate conservation and authentication procedures. Such knowledge arises from reliable documentary sources of technical information contemporary to artists and the preparation of historically accurate reconstructions. Deciphering the words of the past to unravel art technology is far from straightforward, representing one of the most challenging issues within the art conservation field.

Chrome yellow pigment belongs to the 19th century artists' palette. It was enthusiastically used by many artists even when its use was deemed inadvisable. The Portuguese modern painter, Amadeo de Souza-Cardoso, was one of these artists known to have used it.

The aim of this work was the manufacture of chrome yellow pigments with as much historical accuracy as possible. This was the first time the Winsor & Newton 19th Century Artists' Materials Database was systematically explored to support pigment manufacture. The recipes taken from this database were broken down into their relevant steps. This study proposes a correct correspondence between original materials and their current equivalent.

A total of 34 pigments and 3 minerals were characterised by EDXRF, Raman, FTIR, XRD and SEM-EDS. Regardless of the recipe or process variations, lead chromate was identified in the majority of the pigments. Depending on the pH, other compounds were also detected. Basic lead chromate was obtained under alkaline conditions, giving rise to an orange hue. Mixed-crystals of lead chromate and lead sulphate were formed under acidic conditions, presenting a lemon hue. All the extenders used, namely calcite, barytes and gypsum, were detected. Notably, cerussite and calcite were also identified even though they were not added as such during the pigment manufacture.

Moreover, a comparison with case studies samples was performed. Pure lead chromate and mixed-crystals of lead chromate and lead sulphate were identified in the presence of calcite, barytes and cerussite. Proposals concerning the formulation of these pigments are suggested.

A multi-analytical approach proved to be fundamental for the characterisation of all the pigments.

η_{obs}	Observed yield
K_{sp}	Solubility Product Constant
BMC	Best Middle Chrome
BYC	Best Yellow Chrome
CAM-JAP	*Centro de Arte Moderna José de Azeredo Perdigão*
DCC	Dominion Colour Corporation
EDS	Energy Dispersive X-ray Spectroscopy
EDXRF	Energy-Dispersive X-Ray Fluorescence Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
JCPD	Joint Committee on Powder Diffraction Standards
NDCR	*Núcleo do Departamento de Conservação e Restauro*
NWO	Netherlands Organisation for Scientific Research
MNHN	*Museu Nacional de História Natural*
Raman	Raman Spectroscopy
SEM	Scanning Electron Microscopy
SLC	Super Lemon Chrome
W & N	Winsor & Newton
XRD	X-Ray Diffraction

1. Introduction

1.1. Preamble

Modern artists' materials do not represent those used in the past. Current oil paints do not reflect the characteristics of those used by artists of the 19th and early 20th century, such as Columbano Bordalo Pinheiro and Amadeo de Souza-Cardoso. Important properties that affect paint durability and performance have changed profoundly. For instance, due to the demands of the chemical industry, some industrial preparations of pigments involve encapsulation to reduce their chemical reactivity. In addition, different oils and oil processing methods have also been implemented. To understand the technical features of an artwork and solve conservation, provenance and authenticity problems it is essential to perform paint reconstructions with historically accurate materials and recipes [1,2].

Columbano Bordalo Pinheiro and Amadeo de Souza-Cardoso used artists' materials from Winsor & Newton (W & N), one of the main artists' suppliers of the 19th century [3,4]. At the present time, W & N archive is available for research thanks to a project from the De Mayerne Programme[1]: The Winsor and Newton Archive Project. In this project, digital images of handwritten books of recipes and workshop notes dating from 1832 to 1926 were captured and a database with detailed information on the manufacture of pigments, binders and mediums of the 19th century was created [5].

Interest in chrome yellow pigment manufacture arose from a recent study of the Portuguese artist Amadeo de Souza-Cardoso's (1887-1918) palette and paintings. It was discovered that this pigment is ubiquitously present in his works [3].

Research on the W & N database for chrome yellow resulted in a total of 176 records. Four manufacturing recipes were selected as representative. Their reconstruction allows an assessment of the relevance of the information available in the database. Moreover, if a correspondence can be established between the synthesized pigments and samples from oil paint tubes and paintings, these recipes can be considered as historically accurate reconstructions and, most importantly, can be used as reference materials. However, chrome yellow pigment formulation involves more than just the pigment; fillers such as barytes, calcite and gypsum can be also present. To make an appropriate characterisation of these formulations, a multi-analytical approach must be carried out. An overall characterisation of the pigments is achieved by X-Ray Diffraction (XRD), which provides an analysis of the crystal structure, and Scanning Electron Microscopy (SEM) that enables a morphological characterisation [6,7]. In addition, Energy-Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) is used to obtain the elemental composition of the pigments, followed by the fingerprinting techniques, Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR), that provide characterisation at the molecular level [6,8,9]. All of these techniques have been successfully applied in the identification and characterisation of chrome yellow, including in 19th and early 20th century Portuguese paintings [3,7,10-13].

[1] Programme of the Netherlands Organisation for Scientific Research (NWO) on *Molecular Studies in Conservation and Technical Studies in Art History*.

1.2. Chrome Yellow

1.2.1. The Pigment

Nowadays, industrial pigments designated as chrome yellow present a composition with lead chromate ($PbCrO_4$) as the main component or as mixed-crystals with lead sulphate – $Pb(Cr,S)O_4$ – and/or lead molybdate – $Pb(Cr,Mo,S)O_4$[2]. The colour range of these pigments varies from light yellow (containing more lead sulphate) to orange-red (containing more lead molybdate) [14-16]. In the beginning of the 20th century, the lead molybdate pigments were used to substitute the traditional formulations of chrome orange and red pigments (these had been mainly composed of basic lead chromate with the formula $PbCrO_4.xPbO$). In the case of chrome orange, the formula is Pb_2CrO_5[3]. This compound occurs in nature as the rare mineral phoenicochroite [13,17].

Figure 1. Red crystals of crocoite (NDCR FCT/UNL).

Lead chromate occurs naturally as the reddish mineral crocoite (figure 1), discovered in Siberia around 1770. However, its chemical composition was only unveiled in 1797 by L. N. Vauquelin when he isolated and identified the chromium element. In 1809, Vauquelin synthesized lead chromate for the first time, revealing that process modifications would influence the colour. He documented that different pH conditions resulted in different hues: an 'orange yellow' in neutral conditions (pure lead chromate, $PbCrO_4$), 'a yellowish red or sometimes a beautiful deep red' in alkaline conditions (basic lead chromate, Pb_2CrO_5) and a 'deep lemon yellow' in acidic conditions (mixed-crystals of lead chromate and lead sulphate, $Pb(Cr,S)O_4$) [14,18]. Since then, large-scale production of chrome yellow has maintained his essential steps [15]. It is synthesised by adding a solution of a soluble lead salt (nitrate or acetate) to an alkali (generally potassium or sodium) chromate or dichromate solution [14]. The stoichiometric reactions between potassium chromate and dichromate with lead nitrate may be expressed as follows [19,20]:

$$K_2CrO_4\ (aq) + Pb(NO_3)_2\ (aq) \longrightarrow \mathbf{PbCrO_4}\downarrow + 2KNO_3\ (aq) \qquad \text{[eq.1]}$$

$$K_2Cr_2O_7\ (aq) + 2Pb(NO_3)_2\ (aq) + H_2O\ (l) \longrightarrow 2\mathbf{PbCrO_4}\downarrow + 2KNO_3\ (aq) + 2HNO_3\ (aq) \qquad \text{[eq.2]}$$

During the first half of the 20th century, pigment manufacturers concentrated their research on developing and improving chrome yellow properties, without sacrificing its colouristic properties. Stabilizing after-treatments such as surface treatments (also called coating and encapsulation treatments) have been developed [15,16,19,21]. These treatments consist of coating the individual pigment particles with inorganic or organic compounds of low solubility by precipitating them onto the particle surface, limiting the reactions between the pigment and the binder matrix. The most common is by depositing dense amorphous silica onto the pigment surface [15].

From the 1970s onwards, lead chromate-based pigment production has been reduced due to the restrictive legislation concerning health and environmental hazards associated with lead and

[2] A mixed-crystal is a solid solution, i.e., is a crystalline structure in which one or more atoms are substituted by others that can assume the same geometry, without changing the structure. The term mixed-phase pigment is also used [14-16].
[3] The formula $Pb_2(CrO_4)O$ is also used.

chromium(VI) compounds [19,21]. For example, the modern chrome yellow hue oil paints from W & N (Colart Fine Art & Graphics, Ltd.) are organic-based [22]. Nonetheless, owing to its exceptional price-performance ratio, lead chromate pigments are still produced by the paint industry and the improvement of its performance properties is their major concern [16].

Although recognized as a colouring material earlier, its commercial production only began in England between 1814 and 1816 with Dr. Bollman, and few years later in the United States and France following the discoveries of chrome ore mines, especially of chromite ($FeCr_2O_4$) [13,18,23]. Nevertheless, chrome yellow was detected in Thomas Lawrence's (1769-1830) *Portrait of a Gentleman*, dated before 1810 [13,24]. Chrome yellow began to be used widely as a pigment in watercolours and oil paints from the second quarter of the 19th century onwards. It also appeared under the names: Mineral Yellow, Lemon Yellow (also the name of other chromate pigments namely, barium or strontium chromate), Jaune Minerale and Jaune de Cologne [25]. According to George Field (1835), the latter term corresponded to a *"cheap inferior chrome yellow, unfit for artistic purposes"*[4] [26]. Chrome orange (Pb_2CrO_5) was also available throughout the 19th century but its use was not as wide as chrome yellow [13,24]. Even so, this pigment has been found in artists' boxes and its presence in 19th paintings has been detected [7,11]. This pigment was also known as Persian Red, American Vermilion, Chrome Cinnabar and Chrome Scarlet among other terms [13,14]. The availability of colours associated with lead chromate in oil paint tubes and powder, from the English artists' colourmen: W & N, Reeves and Rowney, is given in table 1 [25]. The lack of reliability of 19th century artists' materials labels has also been documented [7,10].

Table 1. Availability of colours associated with lead chromate based pigments in oil paint tubes and powder, from W & N, Reeves and Rowney. From Carlyle, L. (2001). *The Artist's Assistant*. Appendix 26, Tables 6-8.

		Tube First Appearance	Powder First Appearance
Winsor & Newton Colours	Lemon Yellow	1835	1835
	Chrome Yellow	1835	1835
	Chrome Deep	*c.* 1840	*c.* 1840
	Chrome Orange	*c.* 1840	*c.* 1840
	Chrome Scarlet	*c.* 1840[5]	*not in powder*
	Chrome Red	1864	1864[6]
	Chrome Lemon	*c.* 1886	*c.* 1889
Reeves Colours	Lemon Yellow	1852	(1856)
	Chrome Yellow 1, 2, 3 [or pale, middle & deep]	1852	(1856)
	Chrome Orange	1892	*c.* 1898
	Chrome Red	1892[7]	*not in powder*
Rowney Colours	Lemon Yellow	1849	1849
	Chrome Yellow Nos 1, 2, 3 [lemon, yellow, orange] (1855: added No. 4 'deep')	1849	1849

[4] George Field (1777-1854) was a 19th century chemist and artists' colour manufacturer, whose work is one of the most important sources of information for artists' pigments of this period [25].
[5] Chrome Scarlet Powder Last Appearance (W & N): c. 1840 [25].
[6] Chrome Red Powder Last Appearance (W & N): 1876 [25].
[7] Chrome Red Tube Last Appearance (Reeves): 1892 [25].

Because lead chromate possesses high tinting strength, it is known that manufacturers extended their yellow pigments and paints incorporating other inorganic materials such as calcite, calcium sulphate, barium sulphate, clay, lithopone and alumina, either to make the pigments cheaper or improve the mechanical properties or shade [7,10,13,23].

Lead chromate pigment's performance was an object of great discussion by 19th century chemists and artist's colourmen as well as by artist's themselves. The general opinion was that these pigments were of poor stability with a great tendency to fade and discolour in polluted sulphurous atmospheres, and that mixture with Prussian or Antwerp blue should be avoided since it also changed these colours. Some authors even stated that chrome yellow should be prohibited [25]. However, due to the *"pureness, beauty and brilliancy of their colours"* [26], and against all recommendations, chrome yellow pigments continued to be used throughout the century and afterwards [23-25]. Lead chromate-based pigments have been found in paintings from the 19th and 20th centuries, in yellow, orange and green paints (especially mixed with Prussian blue) [3,11,13,23,24]. Vincent Van Gogh's paintings are the perfect example of an unremitting use of chrome yellow. The degradation of chrome yellow pigments is a focus of research at the Van Gogh Museum, as it is still not completely understood. Due to the detection of Cr^{III} compounds (such as Cr_2O_3) on model and real samples, it has been suggested that it amounts to a reduction of the valence state of chromium (VI) to (III) [16,27-28]. On the other hand, no degradation processes involving chrome yellow have been reported in Constable's paintings. Constable started using this pigment since the beginning of its commercialisation, since it appears for the first time in *'The Wheatfield'*, which was shown at the Academy in 1816. He especially used chrome yellow for 'finishing' touches [29]. Furthermore, no evidence of degradation was found in Amadeo's paintings [3].

1.2.2. The Chemistry and Colour

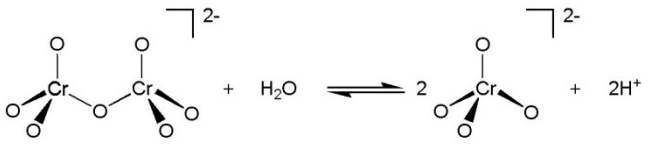
Chromate ion CrO_4^{2-} is an oxo compound of chromium(VI), as is the dichromate ion $Cr_2O_7^{2-}$. Acidification of aqueous solutions of chromate ion initiates a series of labile equilibria between this ion and the dichromate ion. The equilibria are the following [30]:

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K_a = 10^{+0,26} \qquad \text{[eq.3]}$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K_a = 10^{-5,9} \qquad \text{[eq.4]}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ HCrO_4^- \qquad \text{[eq.5]}$$

In solutions above pH 8 the main species is CrO_4^{2-} while between pH 2 and 6 the species $HCrO_4^-$ and $Cr_2O_7^{2-}$ are in equilibrium. The main species at pH below 1 is H_2CrO_4 [30-32]. However, according to some authors, the species $HCrO_4^-$ and H_2CrO_4 do not exist in aqueous solution [33]. The equilibrium between pH 1 and 11 is better expressed by eq.6.



Orange Yellow [eq.6]

Figure 2. Chemical reaction between chromate ion (CrO_4^{2-}) and dichromate ion ($Cr_2O_7^{2-}$) [34].

However, these equilibria are considered very labile and, on the addition of cations such as Ba^{2+}, Pb^{2+} and Ag^{+}, insoluble chromates (instead of soluble dichromates) are formed. Additionally, these equilibria are only established if HNO_3 or $HClO_4$ are used. If HCl or H_2SO_4 are used, other compounds are formed, namely chlorochromate ion and a sulphato complex, respectively [31-33].

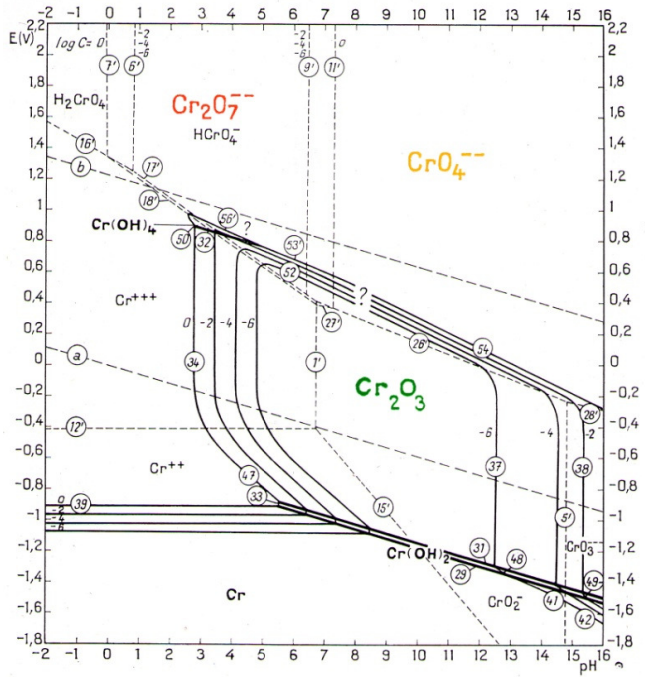


Figure 3. Pourbaix diagram for the Cr-H_2O system at 25ºC [35].

The best way to understand all the reactions involving these ions is using a Pourbaix diagram, which is an electrode potential-pH diagram (figure 3). In summary, the diagram shows the regions where each species is thermodynamically stable. The vertical lines separate species that undergo chemical reactions involving H^{+} (independent of the potential but dependent on the pH), the horizontal lines separate species that undergo electrochemical reactions not involving H^{+} (dependent on the potential but independent of the pH) and the oblique lines separate species that undergo electrochemical reactions involving H^{+} (dependent both on the potential and the pH) [35]. The Pourbaix diagram indicates that between $Cr_2O_7^{2-}$ and CrO_4^{2-} ions occurs a chemical reaction involving H^{+}, being only pH dependent. The species resulting from their oxidation may also be observed, namely Cr^{III} compounds. This supports the theory that chrome yellow degradation processes involve the formation of Cr^{III} compounds [16,35].

Lead chromate exists in two crystal structures, a stable reddish yellow monoclinic structure, space group $P2_1/n$, and a unstable greenish yellow orthorhombic structure, space group P*nma*. Crocoite, like most of the chrome yellow pigments, exhibits the monoclinic structure, as shown in figure 4. Chromate ion has a tetrahedral structure with coordination number 4, as described above, and lead atoms are ionically bonded to the oxygen atoms, with a coordination number equal to 8 [13,36].

Basic lead chromate (phoenicochroite) has a monoclinic structure (figure 5), space group C2/*m*. As in crocoite, the chromate ion has a tetrahedral structure. Lead atoms are ionically bonded to the oxygen atoms of the chromate ion and isolated oxygen atoms, maintaining a coordination number equal to 8 [13,36]. The colour variation between chrome orange and red is due to changes in the particle size, which is related to the degree of alkalinity. A higher degree of alkalinity gives a larger particle size and a deeper red hue [13,21,37].

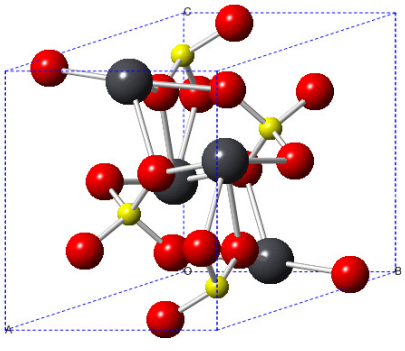


Figure 4. Monoclinic structure of lead chromate (● O; ● Pb; ● Cr).[8]

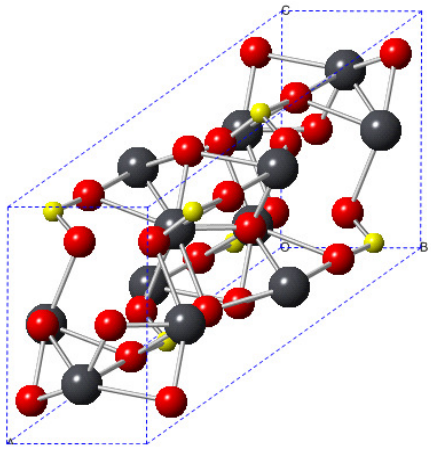


Figure 5. Monoclinic structure of phoenicochroite (● O; ● Pb; ● Cr).[9]

Chromate^{VI} ion is the chromophore responsible for the colour of lead chromate. It is a transition metal oxoanion with d^0 electronic configuration. The colour is due to charge-transfer (CT) transitions from the ligand to the metal. Commonly it involves $p\pi(O) \rightarrow d\pi(Cr)$ electronic transitions. Two main absorption bands are observed at approximately 275 nm and 375 nm (ultraviolet). The edge of the latter band reaches the visible region at around 480 nm (blue), giving rise to the yellow colour of all chromate compounds. For dichromate compounds, the absorption bands shift to longer wavenumbers resulting in its orange colour [38,39].

1.3. The Artists

This work was developed within the framework of the interdisciplinary project "Crossing Borders: the history, materials and techniques of Portuguese painters from 1850-1960". As the title implies, this project aims to uncover the artistic practices of several Portuguese painters by studying their history, materials and techniques. This artistic period was eclectic and consequently, many artistic movements co-existed such as Romanticism, Naturalism and Modernism. Besides the thematic differences, their use of colour and light took different paths [40].

Within the Portuguese painting panorama of this period, two artists emerge with exceptional careers - Columbano Bordalo Pinheiro (1857-1929) and Amadeo de Souza-Cardoso (1887-1917) [40]. Both artists are important case studies from the Crossing Borders project, revealing works that can be considered divergent with the pictorial mainstream of Portuguese art and public taste [40].

In Columbano's long career, he was a master of portrait painting within a solid urban culture, and a Flemish background. Among the Portuguese painters of his time, Columbano did not follow a modern nature relation and his painting process can be considered as an anti-modern statement. His style of using mainly dark colours at the background of his paintings and glowing figures lend a dramatic atmosphere to his works. It reminds one of Rembrandt, Velasquez and Goya, and his quality is undoubtedly brilliant [40].

On the other hand, Amadeo de Souza-Cardoso died young, at the age of 30. During his short career he explored and combined different influences from a variety of sources. As he lived abroad

[8] Crystal structure data from: QUARENI, S; DE PIERI, R. - *A three-dimensional refinement of the structure of crocoite, $PbCrO_4$.* Acta Crystallographica. Vol. 19. 1965. pp. 287-289. (*JCPDS 01-73-1332).*
[9] Crystal structure data from: WILLIAMS, S. A.; McLEAN, W. J.; ANTHONY, J. W. - *A study of phoenicochroite - its structure and properties.* The American Mineralogist. Vol. 55. 1970. pp. 784-792. (*JCPDS 01-76-0861).*

(Paris, Brussels) he was aware of and connected to *avant-garde* artists, groups and movements. His works reflect his interpretation of the *Parisienne* artistic scene. He re-shaped his cultural roots through freely-expressed experimental explorations and produced advanced works for his time [3,40].

1.4. The Winsor & Newton 19th Century Artists' Materials Database

Founded in 1832, W & N expresses a perfect match between science and art in the 19th Century. William Winsor was artistically gifted whereas Henry Newton contributed his scientific knowledge. The company continues to promote *"The World's Finest Artists' Materials"*. W & N was one of the most important artists' colourmen of the 19th century, having supplied many of the leading artists worldwide. The quality of the artists' materials is still their major interest today [5,41].

W & N archive database is a unique primary source, which is now available in the Researchers' Edition. However, to access the database, permission has to be required from W & N directly. It is possible to use the database according to general or specific subjects, one or more at a time. Individual fields can be searched, such as the original title of the recipe or the recipe name interpreted (the subject or title of the recipe expressed in modern terminology). Various topics like pigment manufacture and quality development, or sub-topics covering specific materials such as pigments can also be accessed.

2. Experimental Design

2.1. Researching the Winsor & Newton 19th Century Artists' Materials Database

The W & N database (Researcher Edition) combines a computer-based indexing system with image digitalization of 85 manuscript books (15,003 records) detailing manufacturing practices and recipes for 19th century artists' materials. Nonetheless, 3,579 records are restricted due to the commercial sensitivity of some information.

Research began with the selection of reproducible and representative chrome yellow recipes that W & N would have been using in the second half of the 19th century. From a total of 176 records under the research sub-topic: chrome yellow, four recipes were selected (which also presented clear legible handwriting). All four of the corresponding batches were considered rich and bright by the colourmen themselves, and used different lead sources and extenders. W & N experimented with a variety of extenders including calcite, barytes, plaster of Paris, gypsum, alumina, clay and mixtures (especially of barytes and plaster of Paris). The majority of the 176 recipes, including the ones chosen, are present in books P1 and P2, covering the period between 1846 and 1865, indicating that this was a time of experiments on chrome yellow manufacture.

Aside from the actual recipes, the archive database provides very valuable information about chrome yellows in general, for example this quote from book G3 dated post 1844 (page P018): *"no colour affords perhaps a greater opportunity for adulteration than chrome yellow. When pure it is of such a powerful body and has such strong qualities for staining that it may be adulterated to a great extend without much injuring its appearance as a saleable article (…) and we believe that many of the chromes commonly sold do not contain more than from 30 to 50 per cent of the true colouring matter (…)".*

2.2. Experimental Design

The experimental design developed for this work can be described by the following scheme:

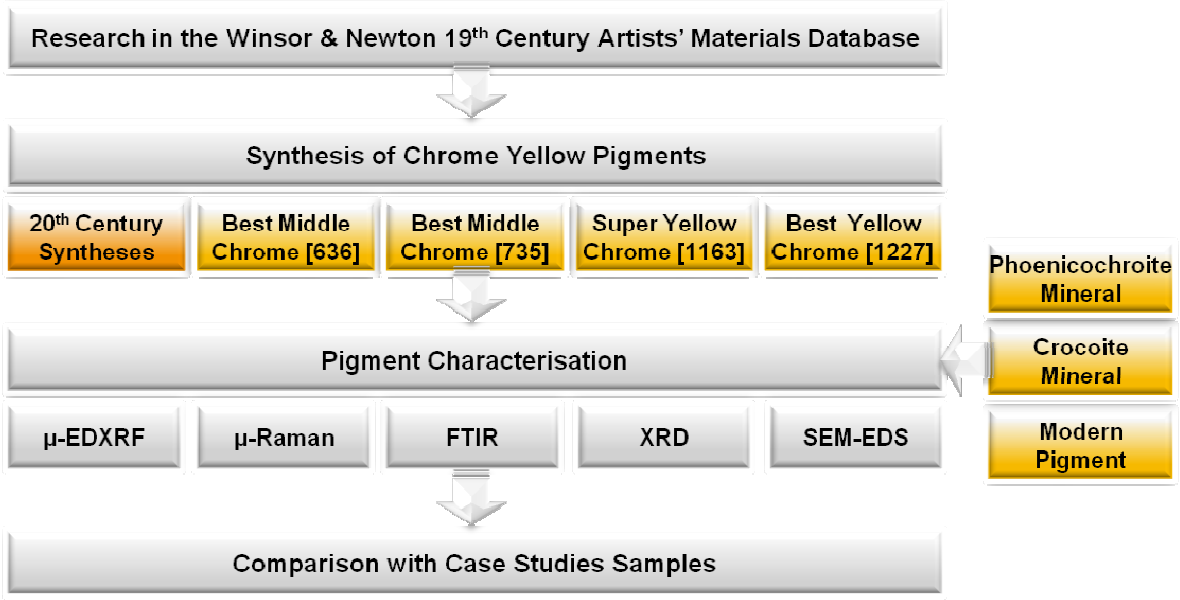


Figure 6. Experimental Design.

Pigment characterisation from six synthesized chrome yellow recipes and four standard samples was performed. Two recipes were in accordance to the stoichiometric reactions [eq.1] and [eq.2] – 20th Century Syntheses - and four were taken from the W & N Database (transcriptions of the latter may be found in appendix I and the scaling down of material quantities from industrial to laboratory scale in appendix II). To facilitate interpretation, W & N recipes are always referred to as shown in figure 6, i.e., with their original name and the number appearing in the margin of the recipe page (marginal numbering). In addition, two approaches for *Best Middle Chrome* [735] were produced, designated [735OH] and [735]. All reagents used, experimental methods and instrumentation are described in appendix III. pH measurements were performed during pigment synthesis and the values obtained for the W & N recipes may be consulted in appendix V.

Reagents used were characterised by Raman (appendix VI) and by FTIR (appendix VII). Additional spectral data were taken from the literature [42,43]. As described above, pigment characterisation was performed by EDXRF, Raman, FTIR, XRD and SEM-EDS. The corresponding data are available from appendix VIII to XII, respectively. The pigments colour was measured using the CIELAB system (where Lab* coordinates correspond to: L* represents the lightness; a* and b* represent the redness-greenness and yellowness-blueness colour dimensions, respectively), the presented values being the average of three measurements. The analytical results obtained for all pigments produced in accordance to each W & N recipe are summarized in tables presented in Appendix VIII.

In order to determine the reproducibility of W & N recipes, three pigments were produced using all ingredients and steps from the original recipe.

3. Results and Discussion

3.1. Standard Samples

To make an accurate characterisation and comparison with the chrome yellow pigments synthesized, samples of crocoite ($PbCrO_4$), phoenicochroite (Pb_2CrO_5) and a modern chrome yellow pigment from Dominion Colour Corporation (DCC) were also characterised. Analysis carried out by Raman and FTIR techniques identified the spectral fingerprints of lead chromate (crocoite) and basic lead chromate (phoenicochroite). XRD analysis was only possible on crocoite (from *Núcleo do Departamento de Conservação e Restauro* - NDCR) and DCC samples, identifying the characteristic x-ray diffraction pattern of lead chromate. XRD analyses on phoenicochroite and crocoite samples (from *Museu Nacional de História Natural* - MNHN) were not possible due to their limited quantity. Furthermore, crocoite was also detected in phoenicochroite micro-sample (see image in figure 7) by μ-Raman. SEM images were only acquired for DCC pigment.

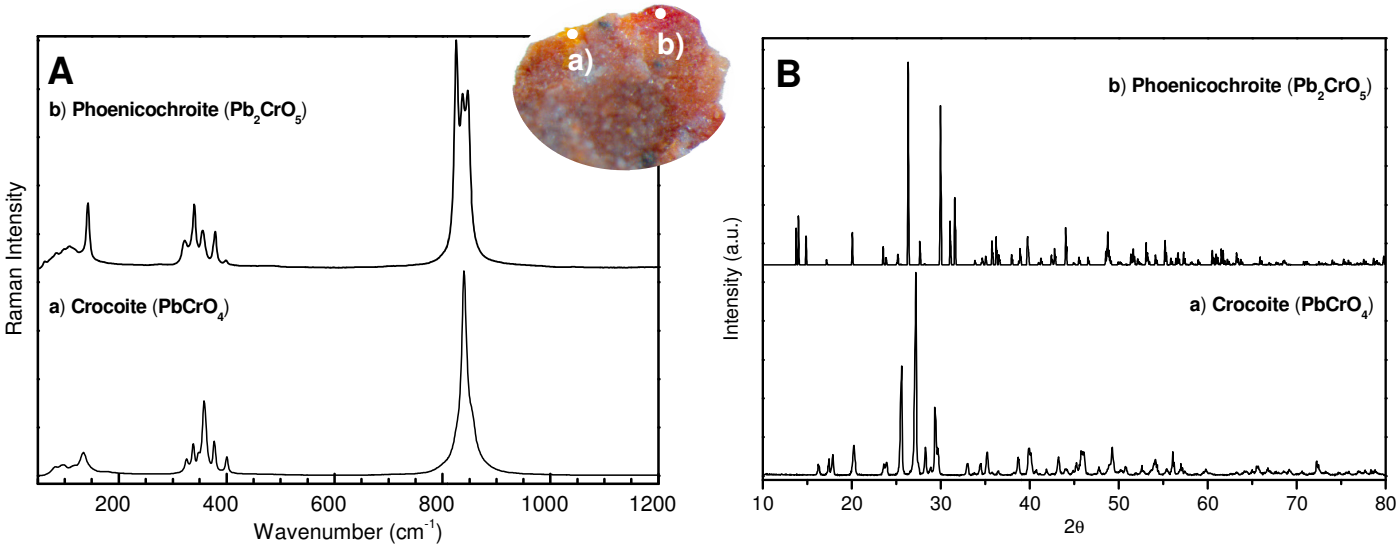


Figure 7. A) Raman spectra of crocoite and phoenicochroite. On the top right, an optical microscopy image of phoenicochroite micro-sample (115x objective). **B)** Diffractograms of crocoite from NDCR (JCPDS[10]: 01-73-1332) and phoenicochroite[11].

Crocoite and DCC samples display similar Raman spectra (figure 7A). The most intense band in Raman spectra is observed at 839 cm^{-1} and is assigned to the ν_1 CrO_4^{2-} symmetric stretching mode. It also shows a series of bands at 325, 337, 357, 375, 399 cm^{-1} that are assigned to the ν_2 and ν_4 CrO_4^{2-} bending modes, and a band at 135 cm^{-1}, attributable to a lattice mode [36]. Phoenicochroite displays a Raman spectrum distinct from crocoite (figure 7A). Raman spectrum shows a very strong band at 825 cm^{-1}, assigned to the ν_1 CrO_4^{2-} symmetric stretching mode, and two strong bands at 837 and 846 cm^{-1}, assigned to the ν_3 CrO_4^{2-} asymmetric stretching mode. In the bending region, Raman spectra displays bands at 322, 341, 355, 379 and 399 cm^{-1}, attributable to ν_2 and ν_4 CrO_4^{2-} bending modes. PbO modes were detected at 144 cm^{-1} and partially overlap the CrO_4^{2-} bending region [36,44].

All the diffraction peaks (figure 7B) of crocoite (NDCR) were indexed to a pure monoclinic phase (space group: $P2_1/n$ (14)) of lead chromate ($PbCrO_4$) with lattice parameters a = 7.12 Å, b = 7.43 Å, c = 6.79 Å, β = 102.4º and Z = 4. These are in line with the literature values (JCPDS: 01-73-1332).

[10] JCPDS is the acronym for Joint Committee on Powder Diffraction Standards.
[11] http://rruff.info/Phoenicochroite/R050587.

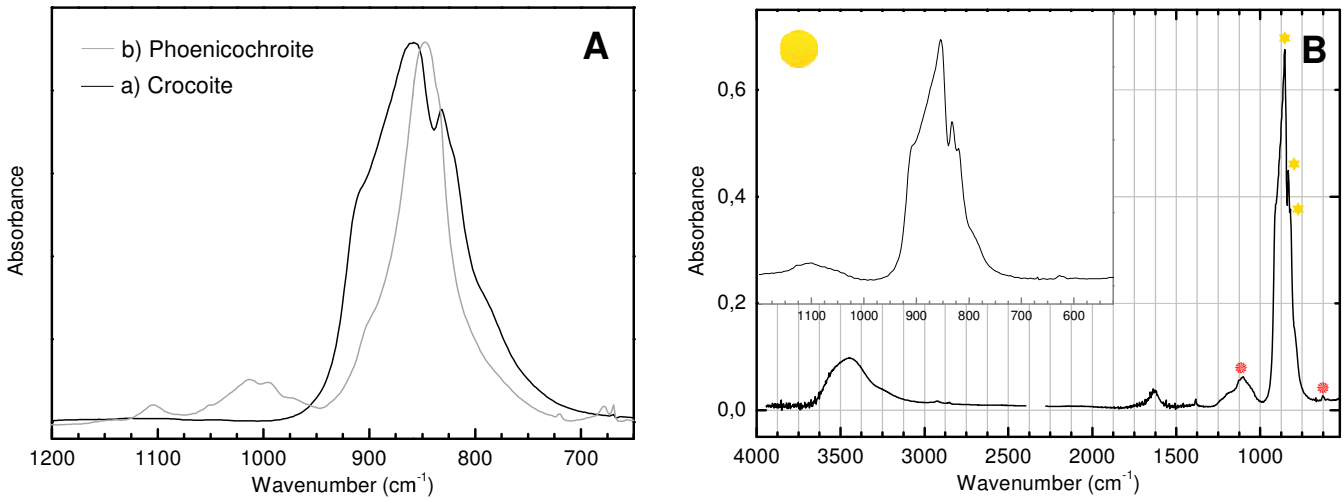


Figure 8. FTIR spectra of **A)** crocoite and phoenicochroite, between 1200 and 650 cm^{-1}, and **B)** DCC sample. Inset: between 1200 and 525 cm^{-1}. ✸ $PbCrO_4$, ✸ $Pb(Cr,S)O_4$.

As may be observed from figure 8A, FTIR spectra of crocoite and phoenicochroite are also distinct. FTIR spectrum of crocoite shows an intense and broad band around 855 cm^{-1} and a shoulder at 831 cm^{-1}, both assigned to the CrO_4^{2-} asymmetric stretching. FTIR spectrum of phoenicochroite exhibits a sharper band at 847 cm^{-1}, without shoulders, also assigned to the CrO_4^{2-} asymmetric stretching.

In FTIR spectrum of DCC pigment (figure 8B), assignment to the CrO_4^{2-} asymmetric stretching is at 854 cm^{-1} and its profile has a better defined structure, triply degenerate. Moreover, it also displays a weak and broad band at 1101 cm^{-1} and a very weak band at 627 cm^{-1}, assigned to the SO_4^{2-} asymmetric stretching and bending, respectively. These are due to the presence of mixed crystals of lead chromate and lead sulphate. These mixed-crystals probably resulted from the addition of sodium sulphate during the pigment manufacture. According to the literature, the lead environment hardly changes with substitution of chromium (Cr) by sulphur (S) cations, while the cation-oxygen bond distances expand to accommodate the larger cations. The valence state of lead cations remains +2 and of chromium and sulphur atoms remains +6 [45]. Only when sulphur atoms are introduced in sufficient quantities in a mixed crystal with chromium atoms, does a phase transition from the monoclinic to an orthorhombic structure take place [16]. This was not the present case, since the diffractogram was indexed to a pure monoclinic phase of $PbCrO_4$. Nonetheless, slight shifts are observed (see figure XII.1; appendix XII; page A.33), suggesting the substitution of some lead atoms by sulphur atoms.

In terms of morphology, SEM analysis allowed the identification of lead chromate rod-like particles, as may be observed in figure 9a).

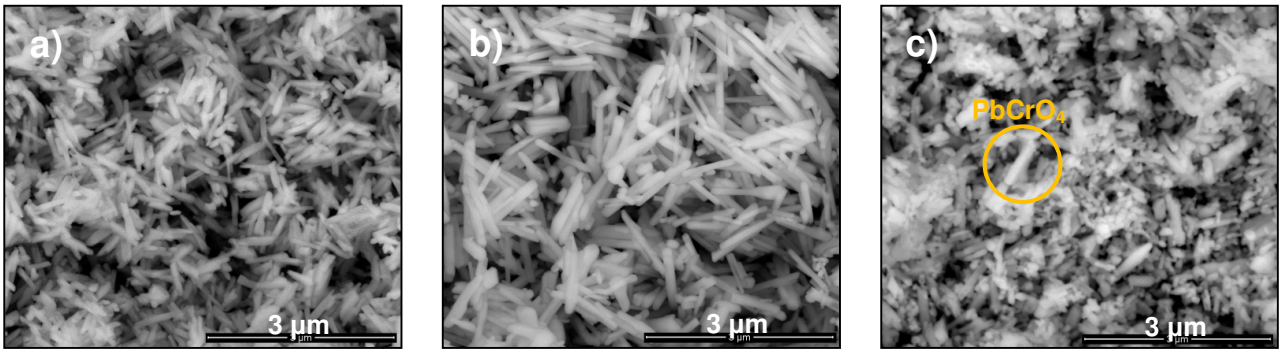


Figure 9. SEM images in BSE mode of **a)** DCC pigment, **b)** SP.1 pigment and **c)** [BMC.735OH].1 pigment.

SEM analysis was also performed to characterise extender particles (figure 10). Gypsum (calcium sulphate dihydrate, $CaSO_4.2H_2O$) particles present a rough and elongated shape of large dimensions. Calcite (calcium carbonate, $CaCO_3$) particles are characterised by their rough appearance, irregular shape and bigger dimensions. On the other hand, the commercially refined barytes (barium sulphate, $BaSO_4$) particles are aggregated, exhibiting a rounded shape and smaller dimensions.

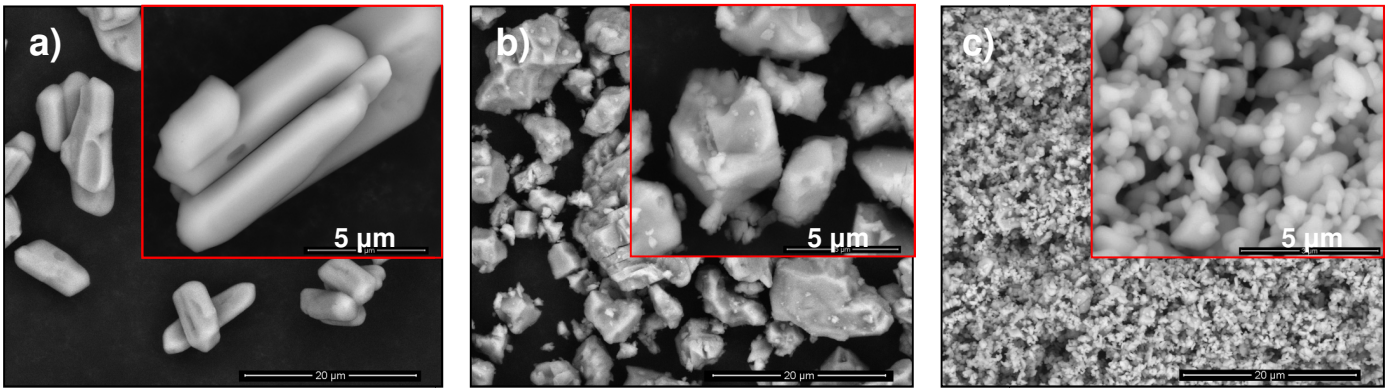


Figure 10. SEM image in BSE mode of **a)** $CaSO_4.2H_2O$, **b)** $CaCO_3$ and **c)** $BaSO_4$.

3.2. 20th Century Syntheses

Two pigments were synthesized in accordance to the stoichiometric reactions [eq.1] and [eq.2]. Their designations are SP.1 and SP.2, respectively. A solution of lead nitrate was added to a solution of potassium chromate and to a solution of potassium dichromate, in SP.1 and SP.2 pigment, respectively. The analytical results obtained for both pigments are summarized in table 2.

Lead chromate was formed in both experiments with a very good reaction yield[12] above 90%. Raman spectra and diffractograms obtained for both pigments are the same, identifying monoclinic lead chromate. FTIR spectra of both pigments are also very similar, displaying an intense and broad band, triply degenerate, at 852 cm^{-1} and 859 cm^{-1}, respectively, assigned to the CrO_4^{2-} asymmetric stretching. However, the CrO_4^{2-} asymmetric stretching profiles are slightly different and SP.1 shows a better defined structure.

Notably, SP.1 pigment shows larger rods than DCC pigment (see figure 9b)), which is probably due to manufacturing differences.

Table 2. Analytical results obtained by colorimetry, EDXRD, Raman, FTIR and XRD for SP pigments. Final pH and pigment yields are also presented.

	Final pH	η (%)	Lab*	EDXRF†	Raman‡	FTIR**		XRD#
SP.1	4,15	95,41	80,19 24,48 83,61	Pb, Cr	**$PbCrO_4$** *lattice mode*:135 w $\delta(CrO_4^{2-})$: 325 vw, 337 w, 357 m, 375 w, 399 vw $\nu_{as}(CrO_4^{2-})$: 839vs	**$PbCrO_4$** $\nu_{as}(CrO_4^{2-})$	852/832/819 [1:0,71:0,65]	**$PbCrO_4$** (monoclinic)
SP.2	0,98	92,74	78,79 22,56 84,76			**$PbCrO_4$** $\nu_{as}(CrO_4^{2-})$	859/832/819 [1:0,71:0,62]	**$PbCrO_4$** (monoclinic)

† See appendix IX; page A.18.
‡ See figure 7A.
** See figures XI.9 to XI.12; appendix XI; pages A.22. In square brackets are presented the normalized intensities for the peaks.
# See figures XII.2 and XII.3; appendix XII; page A.33.
w (weak); vw (very weak); m (medium); vs (very strong).

[12] Reaction yield of both experiments was determined in accordance to the stoichiometric reactions, considering potassium dichromate as the limiting reagent.

3.3. Reconstructions of 19th Century Winsor & Newton Chrome Yellow Recipes

In all the selected W & N recipes, chrome yellow is obtained by adding a lead solution (lead nitrate or lead subacetate) to a solution of potassium dichromate, in neutral or alkaline conditions. Besides the lead source, the main variable between all recipes is the addition of ingredients such as calcite, barytes and gypsum that may be considered as extenders. The fundamental steps of the syntheses are represented by the following scheme:

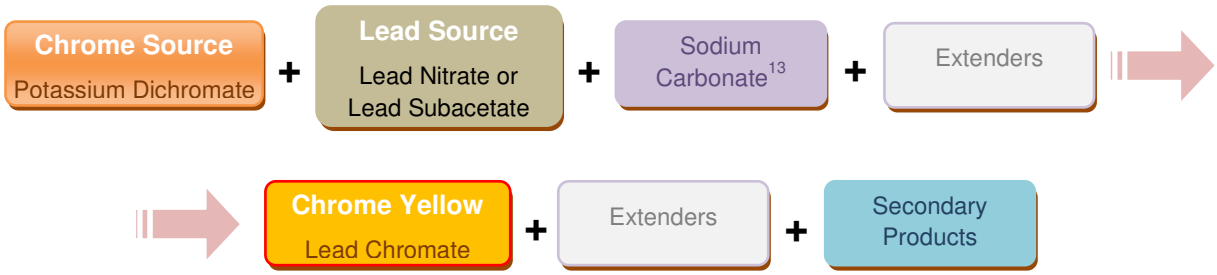


Figure 11. Fundamental steps of W & N chrome yellow syntheses.

As can be seen, in the selected W & N recipes, potassium dichromate is always used as chrome source and sodium carbonate[13] is also always present. By adding sodium carbonate (a pH buffer that maintains a neutral pH) the orange dichromate solution turns yellow around pH 6, indicating the conversion to a chromate solution; see [eq.6] and Pourbaix Diagram (figure 3). The main differences between the recipes are described in table 3.

Table 3. Main differences between the selected W & N chrome yellow recipes.

Recipe	Lead Source	Extenders	Other Ingredients
Best Middle Chrome [735]	Lead nitrate†	Calcite	
Best Middle Chrome [636]	Lead subacetate‡	Barytes	Sulphuric acid
Super Lemon Chrome [1163]	Lead nitrate	Gypsum	Sodium sulphate
Best Yellow Chrome [1227]	Lead subacetate	Gypsum	Sulphuric acid

†Lead nitrate solution is prepared by reacting litharge (PbO) with nitric acid (HNO_3) in an aqueous solution.
‡Lead subacetate solution is prepared by mixing litharge (PbO) and lead acetate ($Pb(Ac)_2.3H_2O$) in boiling water. According to the literature, an aqueous solution of lead subacetate ($Pb(Ac)_2.2Pb(OH)_2$) is thus obtained [46].

Since this was the first time the 19th century W & N chrome yellow recipes were reconstructed in such detail, all recipes were broken down into their relevant steps, i.e., potassium dichromate was mixed with the lead source and with the other possible ingredients individually. Pigment precipitation always occurred. Moreover, three pigments were also produced by using all ingredients and steps from the original recipes. An overall characterisation of the pigments from the complete recipes may be consulted in table 4. Analytical results of all pigments are presented in tables VIII.1-VIII.5 (appendix VIII; pages A.14-A.17) for each recipe.

In all pigments from the complete recipes the final pH ranged from 5 to 8, and lead chromate was the main component. Phoenicochroite was only detected in small amounts when the lead source was lead subacetate. Mixed-crystals of lead chromate and lead sulphate were only identified when

[13] In the original recipe, sodium carbonate is referred only as "soda". In current chemical terminology, this could be the latter compound but also sodium hydroxide. To determine its actual composition, two approaches for *Best Middle Chrome* [735] recipe were carried out. In *Best Middle Chrome* [735OH] the term "soda" was interpret to be sodium hydroxide and in *Best Middle Chrome* [735] to be sodium carbonate. The first trial resulted in pigments mainly composed of phoenicochroite, characteristic of chrome orange pigments. On the other hand, the use of sodium carbonate resulted in chrome yellow pigments. This matter is further developed in the following section: 3.3.1. Best Middle Chrome [735].

sulphuric acid was added. The presence of sodium carbonate promotes the formation of lead carbonate. Furthermore, calcium carbonate is also obtained when gypsum is added, in the presence of sodium carbonate.

Concerning the recipes reproducibility, pigment formulations show quantitative differences between the pigment, extenders and secondary products that may be explained by pH variations during the syntheses. This is frequent when strong acids such as nitric and sulphuric acids are used.

Additionally, it is also important to note that pigments obtained from intermediary steps are also mostly composed of lead chromate, exhibiting colouristic properties.

Each recipe step can be represented by a chemical reaction. This creates a complex network of chemical reactions difficult to break down into the individual chemical equations. Consequently, the presented yields are considered observed yields[14], η_{obs}, being only indicative of the final product quantity and not the effectiveness of the reaction.

Table 4. Overall characterisation by colorimetry, EDXRD, Raman, FTIR and XRD of the pigments from the complete recipes.

	Unique Code	Lab*	EDXRF	Raman	FTIR		XRD
[BMC.735]	[BMC.735].4	82,50 23,03 89,32	Pb, Cr, Ca	**$PbCrO_4$** *lattice mode*:134 w *$\delta(CrO_4^{2-})$:* 325 vw, 337 m-w, 347 w, 357 m, 375 w, 399 vw *$\nu_{as}(CrO_4^{2-})$:* 839 vs **$CaCO_3$** 281 vw, 711 vw, *$\nu_s(CO_3^{2-})$:* 1085 vw **$PbCO_3$** *$\nu_s(CO_3^{2-})$:* 1052 vw	**$Pb(NO_3)_2$** *$\nu_{as}(NO_3^-)$* **$CaCO_3$** *$\nu_{as}(CO_3^{2-})$* *$\delta_{as}(CO_3^{2-})$* **$PbCO_3$** *$\nu_{as}(CO_3^{2-})$* *$\delta_{as}(CO_3^{2-})$* **$PbCrO_4$** *$\nu_{as}(CrO_4^{2-})$*	1384 m 2511 vw; 1797 vw 1422 vs (br) 875 s; 712 m-w 1400 m (br); 1051 vw 678 vw 839 – 831 s	**$PbCrO_4$** (monoclinic) **$CaCO_3$** (rhombohedral) **$PbCO_3$** (orthorhombic)
	[BMC.735].6	80,93 25,35 85,10					
	[BMC.735].7†	80,38 26,06 83,30					
[BMC.636]	[BMC.636].5	85,83 26,88 78,36	Pb, Cr, Ba	**$PbCrO_4$** *Raman fingerprint* **$BaSO_4$** 450 vw, 460 vw, 616 vw, $\nu_s(SO_4^{2-})$: 987 w	**$BaSO_4$** *$\nu_{as}(SO_4^{2-})$* *$\nu_s(SO_4^{2-})$* *$\delta_{as}(SO_4^{2-})$* **$PbCrO_4$** *$\nu_{as}(CrO_4^{2-})$*	1186 m; 1120 s; 1085 vs 984 w 637 m-w; 611 m 853/831 [1:0,76]	**$PbCrO_4$** (monoclinic) **$BaSO_4$** (orthorhombic) **Pb_2CrO_5** (monoclinic)
	[BMC.636].6	76,84 28,19 73,34					
	[BMC.636].7	77,61 28,33 71,54					
[SLC.1163]	[SLC.1163].5	80,23 29,01 83,70	Pb, Cr, Ca	**$PbCrO_4$** *Raman fingerprint* **$CaSO_4.2H_2O$** 181 vw, 493 vw $\nu_s(SO_4^{2-})$: 1007 w; 1132 vw **$CaCO_3$** *Raman fingerprint*	**$CaSO_4.2H_2O$** *$\nu(HO)$* *δ (H_2O)* *ν_{as} (SO_4^{2-})* *δ_{as} (SO_4^{2-})* **$CaCO_3$** **$PbCrO_4$** *$\nu_{as}(CrO_4^{2-})$*	3404 m-s 1686 vw; 1618 w 1140 m; 1116 m 669 w; 602 w *FTIR fingerprint* 833 – 832 s (sh)	**$PbCrO_4$** (monoclinic) **$CaSO_4.2H_2O$** (monoclinic) **$CaCO_3$** (rhombohedral)
	[SLC.1163].7	80,36 27,51 80,07					
	[SLC.1163].8	80,44 26,42 83,17					
[BYC.1227]	[BYC.1227].5	77,68 29,21 84,31	Pb, Cr, Ca	**$PbCrO_4$** *Raman fingerprint* **$CaSO_4.2H_2O$** *Raman fingerprint*	**$CaSO_4.2H_2O$** **$Pb(Cr,S)O_4$** *ν_{as} (SO_4^{2-})* *δ_{as} (SO_4^{2-})* **$PbCrO_4$** *$\nu_{as}(CrO_4^{2-})$*	*FTIR fingerprint* 1104 m (br) 627 w; 599 w 851/830 [1:0,89]	**$PbCrO_4$** (monoclinic) **$CaSO_4.2H_2O$** (monoclinic) **Pb_2CrO_5** (monoclinic)
	[BYC.1227].6#	78,81 30,78 79,58					
	[BYC.1227].7	78,31 27,98 82,86					

† Lead carbonate was not identified.
# Lead carbonate was formed; probably due to the high quantity of lead solution added.

[14] Observed yield was determined assuming potassium dichromate as the limiting reagent.

As previously mentioned, all the selected W & N chrome yellow recipes were broken down into their relevant steps. The results obtained for each recipe are described in what follows.

3.3.1. Best Middle Chrome [735]

The chemical terminology used in the original recipes is occasionally unclear. In order to determine the composition of "soda", which is present in all the selected W & N chrome yellow recipes, two formulations for *Best Middle Chrome* [735] recipe were carried out. The compounds tested were: sodium hydroxide in *Best Middle Chrome* [735OH] and sodium carbonate in *Best Middle Chrome* [735].

3.3.1.1. Best Middle Chrome [735OH]

Two pigments were synthesized, one corresponding to the complete recipe, which included calcium carbonate – [BMC.735OH].2 – and another made without the addition of calcium carbonate in order to determine the reason for its presence in the original recipe – [BMC.735OH].1. Both pigments exhibit an orange colour. Ingredients used in [BMC.735OH] pigment synthesis, their final pH and observed yield are described in table 5. pH measurements performed throughout the pigments synthesis are presented in table V.1 (appendix V; page A.8). It is possible to observe that the final pH is similar for both pigments but the yield was very different with the addition of calcium carbonate. This implies that it was present to act as an "extender" to increase the pigment yield. The characterisation of these pigments is summarized in table VIII.1 (appendix VIII; page A14).

Table 5. Ingredients used in [BMC.735OH] pigment synthesis, their final pH and observed yield.

Ingredients / Unique code	$K_2Cr_2O_7$	NaOH	$CaCO_3$	$Pb(NO_3)_2$	Final pH	η_{obs}(%)
[BMC.735OH].1	•	•	-	•	**9,01**	**59,63**
[BMC.735OH].2	•	•	•	•	**9,37**	**97,26**

With Raman and XRD phoenicochroite was clearly identified in both of these pigments. Raman spectra are similar to that of figure 7A. Phoenicochroite was identified by XRD as the main component in both pigments. Their diffraction peaks were indexed as a monoclinic phase (space group: C2/*m* (12)) of phoenicochroite (Pb_2CrO_5) with lattice parameters a = 14.001 Å, b = 5.675 Å, c = 7.137 Å, β = 115.217º and Z = 4. These are in line with the literature values (JCPDS: 01-76-0861), and also with those of figure 7B. Monoclinic lead chromate was detected in small amounts by XRD.

In [BMC.735OH].1 and [BMC.735OH].2 pigments FTIR spectra, the CrO_4^{2-} asymmetric stretching band appears at 858 cm^{-1} and 854 cm^{-1}, respectively. The sharp CrO_4^{2-} asymmetric stretching profiles indicate a high content of phoenicochroite (basic lead chromate). At the same time, the shoulder at 835 cm^{-1}, also assigned to the CrO_4^{2-} asymmetric stretching, reveals the presence of lead chromate. Moreover, the CrO_4^{2-} asymmetric stretching band and the CO_2^{3-} asymmetric bending band at 874 cm^{-1} (characteristic of calcium carbonate) overlap in [BMC.735OH].2 pigment. FTIR analysis also identified a small amount of lead nitrate (starting material) in both pigments due to the presence of its characteristic NO_3^- asymmetric stretching at 1384 cm^{-1}.

SEM analysis of [BMC.735OH].1 pigment was performed in order to characterise phoenicochroite particles. These appear aggregated and present a sub-rounded shape, completely diverse from lead chromate rod-like particles, also observable in figure 9c).

Since the resulting pigments have an orange hue and are mostly composed of phoenicochroite, sodium hydroxide was excluded as a candidate for the unspecified soda ingredient in chrome yellow manufacture. However, it is not excluded as hypothesis in the case of chrome orange manufacture.

3.3.1.2. Best Middle Chrome [735]

This recipe was broken down into 4 steps. Ingredients used in [BMC.735] pigment synthesis, their final pH and observed yield are described in table 6. pH measurements performed throughout the pigment synthesis are presented in table V.2 (appendix V; page A.8). [BMC.735].5 pigment includes all ingredients and steps from the original recipe but each of the ingredients was added drop by drop. In all other pigments, ingredients were added at once, one after another. Yellow pigment precipitation occurred under different pH values with different yields from pigment to pigment. The characterisation of these pigments is summarized in table VIII.2 (appendix VIII; page A14).

Table 6. Ingredients used in [BMC.735] pigment synthesis, their final pH and observed yield.

Ingredients / Unique code	$K_2Cr_2O_7$	Na_2CO_3	$CaCO_3$	$Pb(NO_3)_2$	Final pH	η_{obs}(%)
[BMC.735].1	•	-	-	•	**1,15**	**50,27**
[BMC.735].2	•	•	-	•	**3,64**	**108,00**
[BMC.735].3	•	-	•	•	**5,77**	**103,42**
[BMC.735].4	•	•	•	•	**5,68**	**190,42**
[BMC.735].5	•	•	•	•	**8,42**	**83,70**
[BMC.735].6	•	•	•	•	**6,01**	**137,27**
[BMC.735].7	•	•	•	•	**6,70**	**111,12**

Lead chromate was detected in all pigments but the CrO_4^{2-} asymmetric stretching profile identified by FTIR differs from pigment to pigment. A small amount of phoenicochroite was uniquely detected in [BMC.735].2 by XRD. [BMC.735].2 reached a maximum pH of 7,27. FTIR spectrum of this pigment exhibits a peculiar CrO_4^{2-} asymmetric stretching profile that is not related to the presence of phoenicochroite. Furthermore, the presence of calcium carbonate causes an overlap between the CrO_4^{2-} asymmetric stretching band and the CO_3^{2-} asymmetric bending band at 873-875 cm^{-1}. Small amounts of lead nitrate (starting material) were detected only by FTIR in [BMC.735].2, [BMC.735].4 and [BMC.735].6 due to the presence of its characteristic NO_3^- asymmetric stretching at 1384 cm^{-1}.

Lead carbonate forms in [BMC.735].2, [BMC.735].4 and [BMC.735].6. The formation of lead carbonate is readily explained from the similarity between its solubility product constant[15] (K_{sp}=7,4 × 10^{-14}) and that of lead chromate (K_{sp}=1,8 × 10^{-14}). In addition, calcium carbonate has a higher K_{sp}, equal to 3,36 × 10^{-9}, meaning it can contribute with CO_3^{2-} ions to the formation of lead carbonate together with sodium carbonate [47,48]. In FTIR spectrum of [BMC.735].4 and [BMC.735].6, an overlap between the CO_3^{2-} asymmetric stretching bands of calcium carbonate and lead carbonate is also observed.

[15] Solubility product constant is the constant for the solubility equilibrium of a nearly insoluble or slightly soluble ionic compound. The smaller the K_{sp} value, the lower the solubility of the salt [48].

Comparing the composition of the pigments from the complete recipe with [BMC.735].5, it is clear that the rate of addition is an important parameter influencing the final pH and needs to be considered. Due to the analytical results for [BMC.735].5, namely the identification of a mixture of $PbCrO_4$, $K_2Pb_2(CrO_4)_3$ and $CaCO_3$ as the main component, it is suggested that W & N was manufacturing chrome yellow by adding each ingredient all at once, one ingredient followed by another. $K_2Pb_2(CrO_4)_3$ has not, to date been identified in chrome yellow pigments [7]. This compound was formed under alkaline conditions but Pb_2CrO_5 was not detected. $K_2Pb_2(CrO_4)_3$ was easily detected by XRD and, although it was not identified by the spectroscopic techniques, its presence is notable in the CrO_4^{2-} modes of both spectra, FTIR and Raman. XRD analysis was facilitated by previous detection of the K element by EDXRF.

The composition of the pigments from the complete recipe, [BMC.735].4, [BMC.735].6 and [BMC.735].7, presents differences, notably in their colours. The quantity of lead carbonate is variable from pigment to pigment being nonexistent in the latter, [BMC.735].7. As the quantity of lead carbonate decreases, more calcium carbonate is detected and the CrO_4^{2-} asymmetric stretching band becomes more defined. Moreover, pigment yield also decreases.

As may be seen in figure 12, [BMC.735].4, [BMC.735].6 and [BMC.735].7 comprise lead chromate particles of similar shape (rods) but different dimensions are observed. In terms of particle size, the most uniform is [BMC.735].7. Calcium carbonate particles were identified due to the detection of the elements Ca, C and O by Energy Dispersive X-ray Spectroscopy (EDS) coupled to the SEM equipment. It was not possible to identify lead carbonate particles.

These experimental results confirmed sodium carbonate as appropriate for the “soda” ingredient in what concerns chrome yellow manufacture, since lead chromate is the main pigment component.

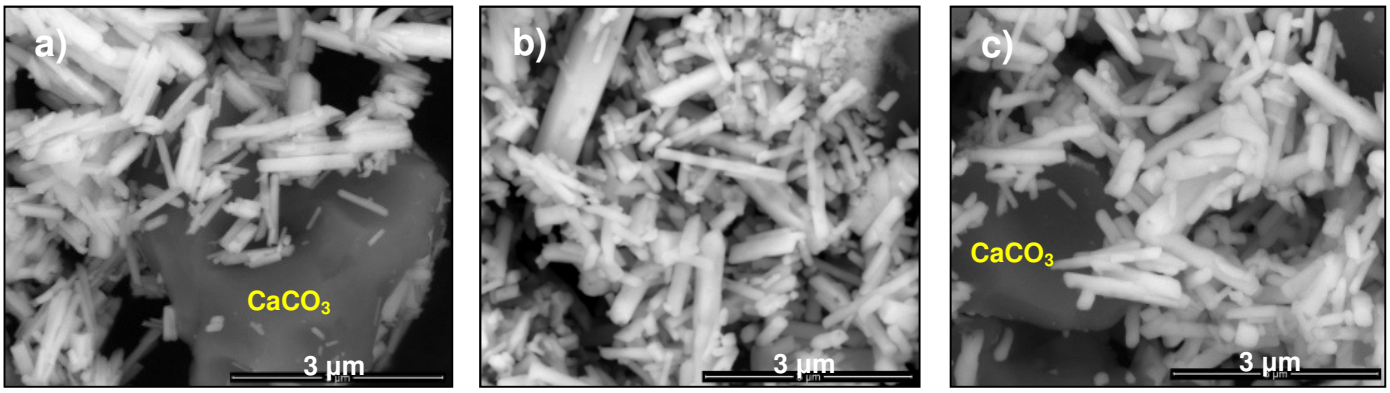


Figure 12. SEM images in BSE mode of **a)** [BMC.735].4 pigment, **b)** [BMC.735].6 pigment and **c)** [BMC.735].7 pigment.

3.3.2. Best Middle Chrome [636]

Similarities between *Best Middle Chrome* [636] recipe and *Best Middle Chrome* [735] are seen in the molar proportions of the starting materials, potassium dichromate and sodium carbonate. The recipe was broken down into 5 steps. Ingredients used in the syntheses, the final pH and observed yield are described in table 7. pH measurements performed throughout the pigment synthesis are presented in table V.3 (appendix V; page A.9).

[BMC.636].5, [BMC.636].6 and [BMC.636].6 pigments include all ingredients and steps from the original recipe. Yellow pigment precipitation occurred under different pH values but, the final pH of the

pigments from the complete recipe was neutral. Notably, all yields are below 100%, even with the addition of barium sulphate (extender). The characterisation of these pigments is summarized in table VIII.3 (appendix VIII; page A.15).

Lead chromate was detected in all pigments, excepting [BMC.636].3 where mixed crystals of lead chromate and lead sulphate were also detected. The CrO_4^{2-} asymmetric stretching profile identified by FTIR differs from pigment to pigment, especially when different lead chromate compounds co-exist.

Table 7. Ingredients used in [BMC.636] pigment synthesis, their final pH and observed yield.

Ingredients / Unique code	$K_2Cr_2O_7$	Na_2CO_3	H_2SO_4	$BaSO_4$	$Pb(Ac)_2.2Pb(OH)_2$	Final pH	η_{obs}(%)
[BMC.636].1	•	-	-	-	•	**6,54**	**46,94**
[BMC.636].2	•	•	-	-	•	**10,90**	**56,01**
[BMC.636].3	•	-	•	-	•	**2,25**	**51,97**
[BMC.636].4	•	-	-	•	•	**6,07**	**78,38**
[BMC.636].5	•	•	•	•	•	**6,63**	**80,75**
[BMC.636].6	•	•	•	•	•	**6,62**	**82,41**
[BMC.636].7	•	•	•	•	•	**6,46**	**78,26**

A small amount of phoenicochroite was detected in [BMC.636].2 by Raman and XRD. This pigment reached a pH of 10,90. Its main component is $K_2Pb_2(CrO_4)_3$, uniquely detected by XRD. Once again, EDXRF analysis was essential. Nonetheless, a Raman spectrum of an unidentified chromate compound (figure 13A) was obtained. It displays a band at 839 cm^{-1}, assigned to the ν_1 CrO_4^{2-} symmetric stretching mode of $PbCrO_4$ and, in the bending region, bands at 341, 357, 376 and 400 cm^{-1} that do not correspond to the ν_2 and ν_4 CrO_4^{2-} bending modes of $PbCrO_4$. Consequently, it can be suggested that this Raman spectrum might correspond to $K_2Pb_2(CrO_4)_3$. FTIR spectrum presents a different and very broad CrO_4^{2-} asymmetric stretching profile that shifts to higher wavenumbers, in comparison with the CrO_4^{2-} asymmetric stretching profile of pure lead chromate.

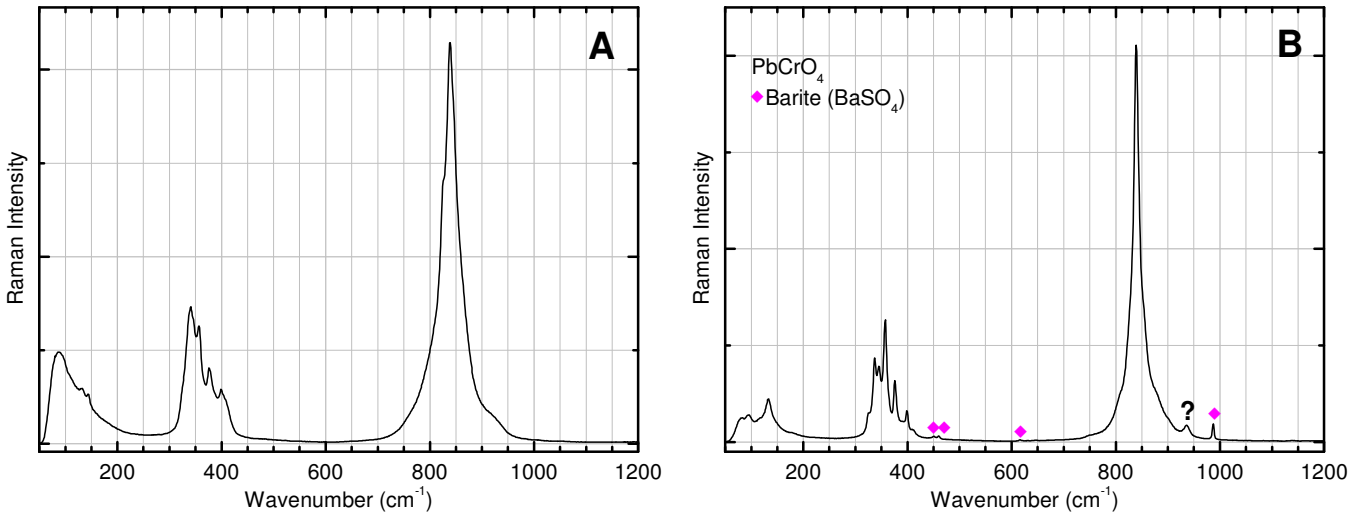


Figure 13. Raman spectra of **A)** [BMC.636].2 pigment and **B)** [BMC.636].4 pigment.

Orthorhombic crystals of lead chromate were uniquely detected in [BMC.636].1 and [BMC.636].4 by XRD. According to the literature, lead chromate in the orthorhombic crystal form is also yellow in colour. Upon precipitation, these crystals are initially formed however since they are thermodynamically unstable they usually convert to the monoclinic form. Nowadays, this conversion is

achieved by increasing the temperature and maintaining an excess of chromate ions [19]. In the present experiments, the temperature and the quantity of chromate ions were kept the same for all, but orthorhombic crystals were only formed in the mentioned pigments, [BMC.636].1 and [BMC.636].4. Its identification by FTIR was not possible since the CrO_4^{2-} asymmetric stretching profile is similar to that of pure monoclinic lead chromate. On the other hand, in Raman spectra there is an intensity shift on the CrO_4^{2-} bending modes of $PbCrO_4$ and an unassigned band appears at 936 cm^{-1}, which can be seen in figure 13B.

Mixed crystals of lead chromate and lead sulphate in the monoclinic form were detected in [BMC.636].3 (figures 15 and 16). This matter is further discussed below, together with [SLC.1163].3.

The pigments from the complete recipe, [BMC.636].5, [BMC.636].6 and [BMC.636].7, present differences at the quantitative level but all have lead chromate and the extender barium sulphate as the main components. These differences influence the pigments' colour. No secondary products or starting materials were detected. Although a small amount of phoenicochroite was detected by XRD, the CrO_4^{2-} asymmetric stretching observed in FTIR spectrum can be assigned only to $PbCrO_4$. The CrO_4^{2-} asymmetric stretching profile has a well defined structure.

As may be observed from figure 14, lead chromate rod-like particles of [BMC.636].5, [BMC.636].6 and [BMC.636].7 pigments show larger dimensions in comparison with those of [BMC.735] pigments (figure 12). Barium sulphate particles were identified by EDS due to the detection of Ba, S and O, presenting a rounded shape and smaller size. Morphological similarities between the latter and phoenicochroite particles, makes it impossible to distinguish them.

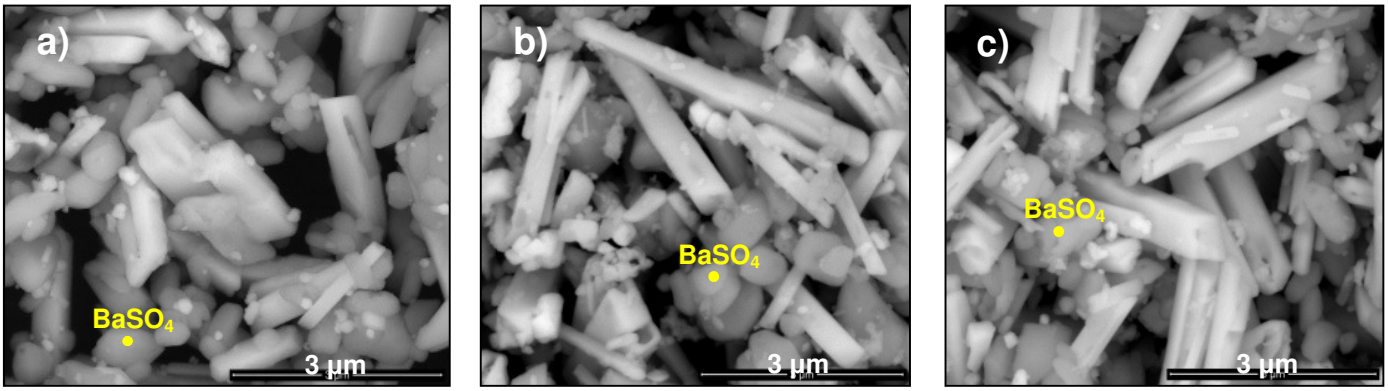


Figure 14. SEM images in BSE mode of **a)** [BMC.636].5 pigment, **b)** [BMC.636].6 pigment and **c)** [BMC.636].7 pigment.

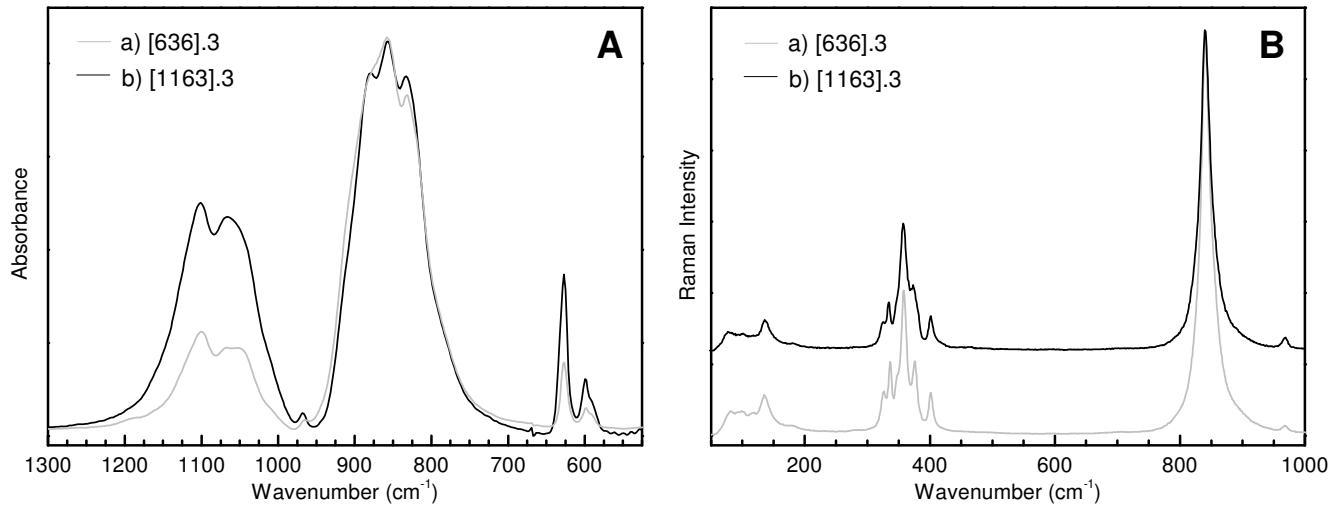


Figure 15. A) FTIR spectra of [BMC.636].3 and [SLC.1163].3 pigments, between 1300 and 525 cm^{-1}. **B)** Raman spectra of [BMC.636].3 and [SLC.1163].3 pigments.

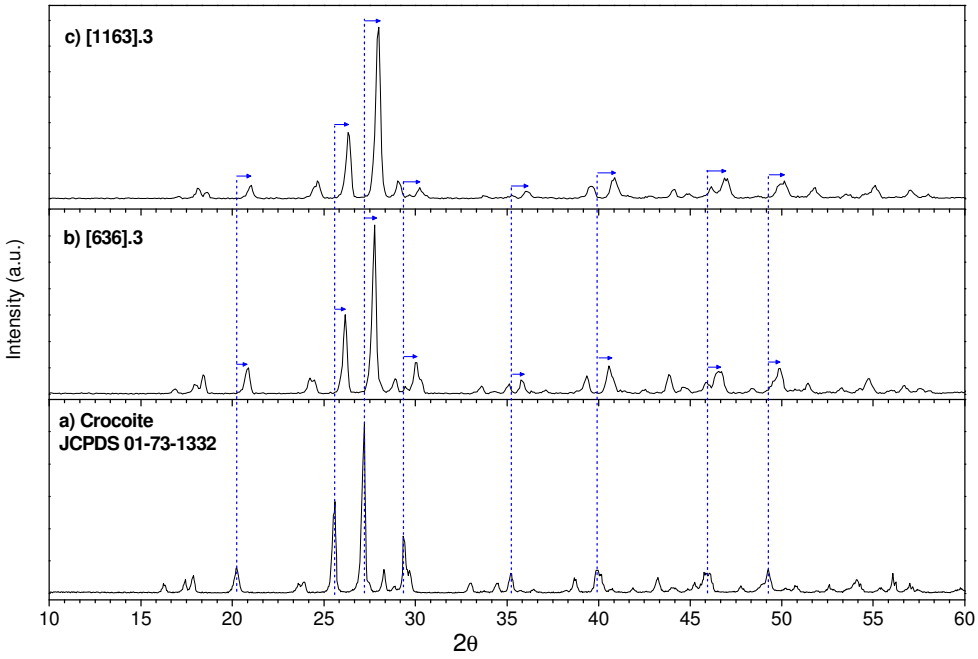


Figure 16. Diffractograms of crocoite (NDCR), [BMC.636].3 pigment and [SLC.1163].3 pigment.

3.3.3. Super Lemon Chrome [1163]

The *Super Lemon Chrome* [1163] recipe calls for a higher quantity of sodium carbonate (in comparison with the previous recipes). Its process was broken down into 5 steps. Ingredients used in the syntheses, the final pH and observed yield are described in table 8. Lead solution volume is not clear in the process description. In [SLC.1163].5 (as in [SLC.1163].7 and [SLC.1163].8) 9,7 ml of lead solution were added whereas in [SLC.1163].6 15 ml were added. pH measurements were performed throughout the pigment synthesis and are presented in table V.4 (appendix V; page A.9). Extenders were added after pigment precipitation, as directed in the original recipe.

Yellow pigment precipitation occurred under acidic and neutral conditions. The characterisation of these pigments is summarized in table VIII.4 (appendix VIII; page A.16). Lead chromate was detected in all pigments, with the exception of [SLC.1163].3. No other lead chromate compound was detected.

Lead carbonate was formed in [SLC.1163].2 as in [BMC.735].2 and [BMC.735].4. As mentioned, this is due to the similarity between its solubility product constant and that of lead chromate [47,48]. Notably, [SLC.1163].2 exhibits the higher yield. Its FTIR spectrum shows a CrO_4^{2-} asymmetric stretching profile poorly defined, similar to [BMC.735].2. Nevertheless, lead carbonate was not detected in any of the pigments from the complete recipe.

Table 8. Ingredients used in [SLC.1163] pigment synthesis, their final pH and observed yield.

Ingredients / Unique code	$K_2Cr_2O_7$	Na_2CO_3	Na_2SO_4	$Pb(NO_3)_2$	$CaSO_4.2H_2O$	Final pH	η_{obs}(%)
[SLC.1163].1	•	-	-	•	-	**1,02**	**98,29**
[SLC. 1163].2	•	•	-	•	-	**7,71**	**155,71**
[SLC. 1163].3	•	-	•	•	-	**1,18**	**100,81**
[SLC. 1163].4	•	-	-	•	•	**1,67**	**104,87**
[SLC. 1163].5	•	•	•	•	•	**7,82**	**101,15**
[SLC. 1163].6	•	•	•	•	•	**7,48**	**73,07**
[SLC. 1163].7	•	•	•	•	•	**7,31**	**125,74**
[SLC. 1163].8	•	•	•	•	•	**7,42**	**110,36**

All the fingerprinting techniques clearly detected mixed crystals of lead chromate and lead sulphate in [SLC.1163].3. As in [BMC.636].3, this occurred under acidic conditions. Sulphate ions were introduced by the addition of sulphuric acid and sodium sulphate in [BMC.636].3 and [SLC.1163].3, respectively. Sulphuric acid and sodium sulphate were added before the lead solution. A higher content of sulphate ions was added in [SLC.1163].3. Comparing the spectra of FTIR, Raman and diffractograms of both pigments is clear that as the content of sulphate ions is higher, the shift from pure lead chromate is larger. In FTIR spectra (figure 15A), identifying the higher content of sulphate ions is straightforward due to the SO_4^{2-} vibrational bands intensity, which are shifted from those of pure lead sulphate. Additionally, the CrO_4^{2-} asymmetric stretching profile also changes. In Raman spectra (figure 15B), the differences appear in the bands intensity in the CrO_4^{2-} bending region, displaying the SO_4^{2-} symmetric stretching band at 968 cm^{-1}. However, no phase transition from the monoclinic to an orthorhombic structure has occurred since both diffractograms were indexed to a pure monoclinic phase of $PbCrO_4$ (JCPDS: 01-73-1332). In figure 16, is possible to observe that as the content of sulphate ions is higher, the shift from crocoites' XRD pattern is larger.

Interestingly, calcium carbonate forms in all the pigments from the complete recipe, [SLC.1163].5, [SLC.1163].6, [SLC.1163].7 and [SLC.1163].8. The formation of calcium carbonate (K_{ps}=3,36 × 10^{-9}) is explained by the higher K_{ps} of calcium sulphate dihydrate ($CaSO_4.2H_2O$) equal to 3,14 × 10^{-5}, which implies that calcium ions were in solution and reacted with the carbonate ions introduced by the addition of sodium carbonate [47]. As the quantity of calcium carbonate increases, the quantity of gypsum decreases, being nonexistent in [SLC.1163].6 and [SLC.1163].8. At the same time, the CO_3^{2-} asymmetric bending band at 874 cm^{-1} becomes sharper, altering the CrO_4^{2-} asymmetric stretching profile. [SLC.1163].5, [SLC.1163].7 and [SLC.1163].8 yields are above 100%.

FTIR spectra of [SLC.1163].5 and [SLC. 1163].6 show similar CrO_4^{2-} asymmetric stretching profiles, displaying an overlap between the CrO_4^{2-} asymmetric stretching and the CO_3^{2-} asymmetric bending. pH values of the corresponding solutions were neutral regardless of lead solution differences.

The differences between the pigments from the complete recipe, [SLC.1163].5, [SLC.1163].7 and [SLC.1163].8 pigments, are also observable in their SEM images (figure 17), which exhibit lead chromate rods of several dimensions. They are occasionally aggregated. Notably, calcium carbonate particles (detection of Ca, C and O by EDS) formed during pigment manufacture present a rounded shape, different from calcium carbonate particles used in [BMC.735] pigment synthesis. Calcium sulphate dihydrate particles were also detected by EDS and by their morphology.

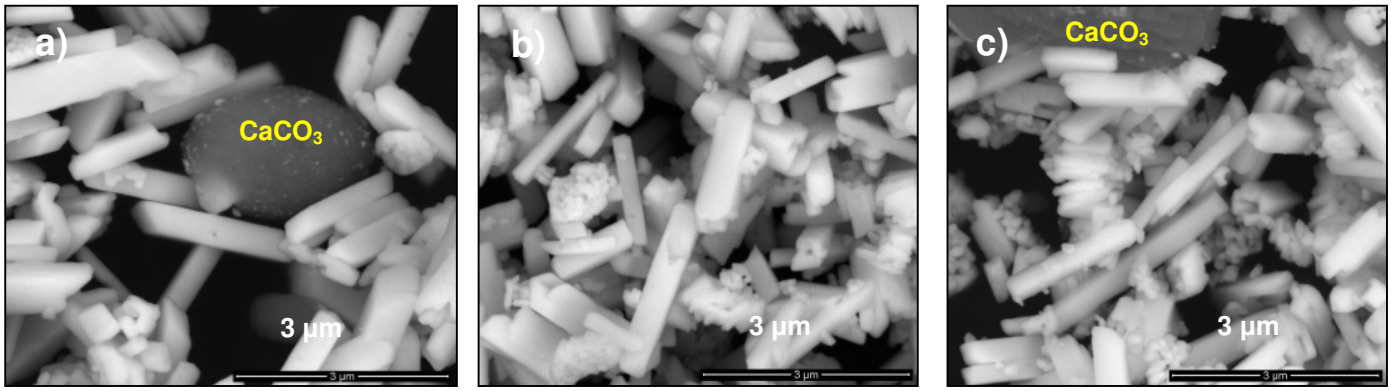


Figure 17. SEM images in BSE mode of **a)** [SLC.1163].5 pigment, **b)** [SLC.1163].7 pigment and c**)** [SLC.1163].8 pigment.

3.3.4. Best Yellow Chrome [1227]

The *Best Yellow Chrome* [1227] recipe includes an intermediate quantity of sodium carbonate (compared with the previous recipes). The recipe was broken down into 5 steps. Ingredients used in the syntheses, the final pH and observed yield are described in table 9. pH measurements were performed throughout the pigment synthesis and are presented in table V.5 (appendix V; page A.9). The volume of lead solution added was variable from pigment to pigment, since the process description states *"strike [1227] with the lead liquor [1229] till neutralized"* (see recipe transcription on page A.2, appendix I). The extender used was gypsum (as in *Super Lemon Chrome* [1163] recipe). [BYC.1227].5, [BYC.1227].6 and [BYC.1227].7 pigments include all ingredients and steps from the original recipe. Pigment precipitation occurred under neutral and alkaline conditions. All pigments exhibit a yellow colour with the exception of [BYC.1227].2, which has a reddish hue. The characterisation of these pigments is summarized in table VIII.5 (appendix VIII; page A.17).

Lead chromate was detected in all pigments, with the exception of [BYC.1227].3. A small amount of phoenicochroite was identified in [BYC.1227].1, [BYC.1227].5 and [BYC.1227].7 by XRD. However, its low quantity is not perceptible by FTIR. The CrO_4^{2-} asymmetric stretching profiles identified by FTIR in [BYC.1227].1, [BYC.1227].4, [BYC.1227].5 and [BYC.1227].7 pigments are similar and resemble to the CrO_4^{2-} asymmetric stretching profile of pure lead chromate.

Table 9. Ingredients used in [BYC.1227] pigment synthesis, their final pH and observed yield.

Ingredients / Unique code	$K_2Cr_2O_7$	Na_2CO_3	H_2SO_4	$Pb(Ac)_2.2Pb(OH)_2$	$CaSO_4.2H_2O$	Final pH	η_{obs}(%)
[BYC.1227].1	•	-	-	•	-	**8,79**	**85,47**
[BYC.1227].2	•	•	-	•	-	**9,96**	**151,56**
[BYC.1227].3	•	-	•	•	-	**6,88**	**101,70**
[BYC.1227].4	•	-	-	•	•	**7,06**	**76,88**
[BYC.1227].5	•	•	•	•	•	**7,32**	**121,44**
[BYC.1227].6	•	•	•	•	•	**7,20**	**118,99**
[BYC.1227].7	•	•	•	•	•	**7,60**	**115,19**

The main component of [BYC.1227].2 is phoenicochroite as detected by all techniques. This compound is responsible for the reddish hue of the pigment. The volume of lead solution added was 13,5 ml and the pH never reached neutral conditions. Additionally, $NaPb_2(CO_3)_2OH$ and monoclinic $PbCrO_4$ were also detected by XRD. FTIR spectrum shows bands at 1437 and 691 cm^{-1}, assigned to the CO_3^{2-} asymmetric stretching and bending, and an intense and broad band at 851 cm^{-1}, assigned to the CrO_4^{2-} asymmetric stretching. The profile of the latter band indicates a high content of phoenicochroite but the shoulder at 835 cm^{-1}, also reveals the presence of lead chromate. In this particular case, EDXRF was not useful since the equipment used does not allow elemental detection below Z = 11, sodium inclusive.

Lead sulphate was formed in [BYC.1227].3 pigment and its identification was possible by FTIR, Raman and XRD. To neutralize the solution, 38,5 ml of lead solution were added. The solution never reached alkaline conditions but the other compound detected by XRD and Raman was phoenicochroite. However, Raman spectrum shows differences in the CrO_4^{2-} stretching and bending regions, comparing with the characteristic spectrum of phoenicochroite (figure 7A). Furthermore, the

FTIR spectrum also displays SO_4^{2-} vibrational bands at 965, 626 and 599 cm^{-1} that do not correspond to those of pure lead sulphate. This is probably due to the formation of mixed crystals of phoenicochroite (basic lead chromate) and lead sulphate.

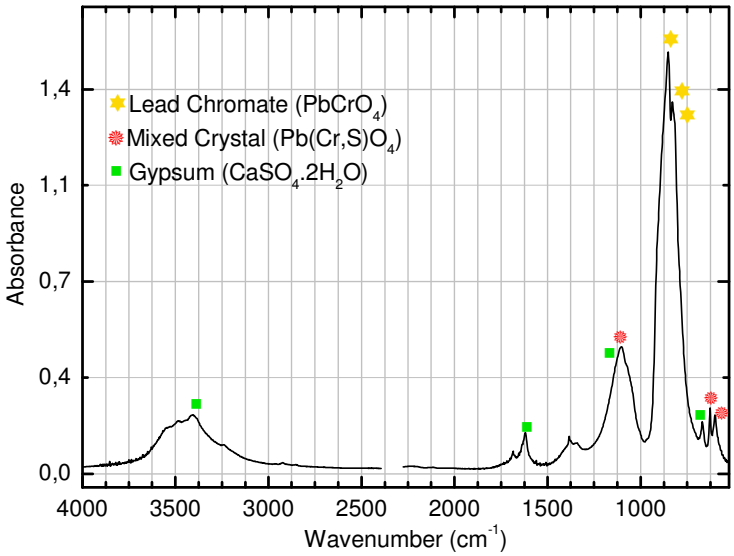


Figure 18. FTIR spectrum of [BYC.1227].5 pigment.

[BYC.1227].5 and [BYC.1227].7 pigments have lead chromate as the main component. They yield over 100% for the complete recipe. The extender used was gypsum and it was detected by FTIR, Raman and XRD. However, calcium carbonate was not formed as in *Super Lemon Chrome* [1163] recipe. This is readily explained by the gas liberation (CO_2) that resulted from the addition of sulphuric acid. This eliminated all the existing carbonate ions. The volume of lead solution required to neutralize the pigment solution was 13,5 ml for [BYC.1227].5 and 20 ml for [BYC.1227].7. Mixed crystals of lead chromate and lead chromate were also formed. [BYC.1227].5 FTIR spectrum (figure 18) displays bands at 1101, 626 and 599 cm^{-1}, attributable to the SO_4^{2-} asymmetric stretching and bending, respectively. The differences in lead solution volume may explain the morphological differences between lead chromate particles for both pigments (figure 19). These particles show a more angular shape than all the other pigments, especially [BYC.1227].7, which also presents larger particles. It is suggested that a more angular shape may be related to the substitution of Cr atoms by S atoms. However, this is not observed in DCC pigment particles, which has a low content of mixed crystals. In the SEM image of [BYC.1227].5 pigment, it is also possible to see a phoenicochroite sub-rounded particle, which was identified by its morphology and elemental analysis by EDS that detected Pb, Cr and O elements.

The volume of lead solution necessary to neutralize the [BYC.1227].6 solution was over 30 ml, which means that the reproducibility issue may be centred on the preparation of lead solution, at least in this case. Due to the high amount of lead introduced during pigment manufacture, lead carbonate was formed and its detection was possible by all techniques, except by Raman. Moreover, as in other pigments where lead carbonate was identified, the CrO_4^{2-} asymmetric stretching FTIR profile is poorly defined. In SEM analysis, lead carbonate particles were identified due to the detection of Pb, C and O elements by EDS.

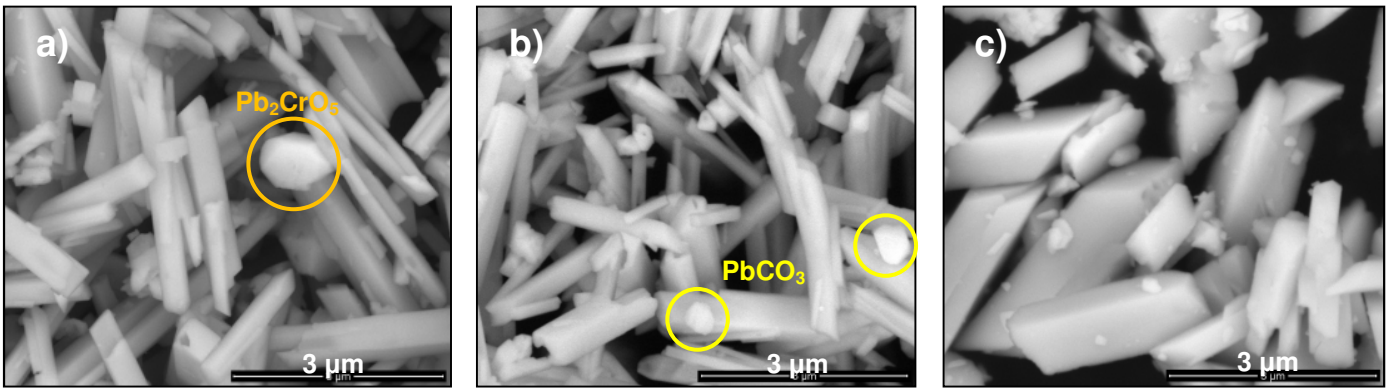


Figure 19. SEM images in BSE mode of **a)** [BYC.1227].5 pigment, **b)** [BYC.1227].6 pigment and **c)** [BYC.1227].7 pigment.

3.4. Case Studies

Samples of artist's materials and paintings assigned to Columbano Bordalo Pinheiro and Amadeo de Souza-Cardoso were analysed by µ-EDXRF, µ-Raman and µ-FTIR. Columbano's chrome yellow oil paint tubes bear W & N labels. Amadeo's samples also comprise two chrome yellow oil paint tubes (figure 20), one from Lefranc's (French artist's colourman) and another from an unidentified colourman. Additionally, a yellow micro-sample from a paint box attributed to Amadeo (from *Centro de Arte Moderna José de Azeredo Perdigão (CAM-JAP)* Collection) and two green micro-samples from Amadeo's painting: *Mucha*, were analysed. It is known that Amadeo made his greens by mixing Prussian blue, ultramarine blue, viridian and chrome yellow [3]. See figure 20.

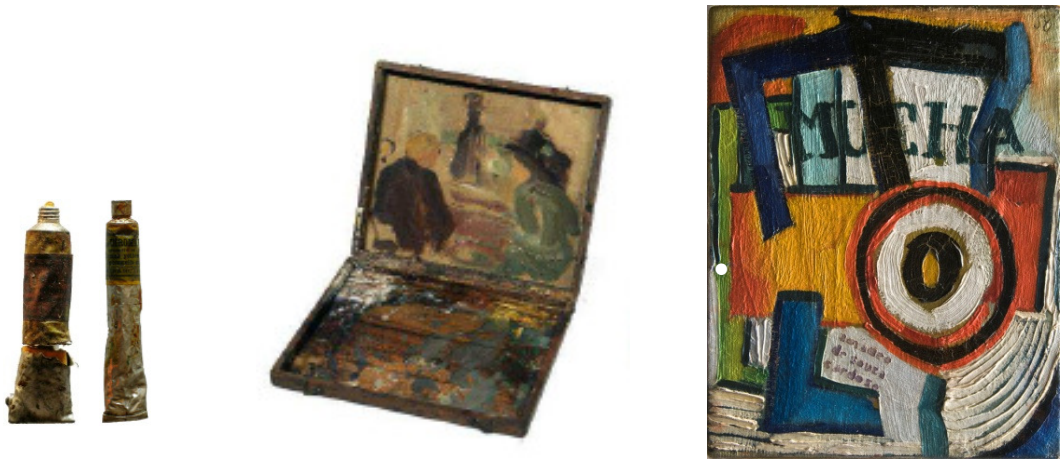


Figure 20. On the left**,** Amadeo's oil paint tubes ASC2 and ASC17; on the center, Amadeo's paint box (CAM-JAP) and on the right, Amadeo's painting: *Mucha* (1915-1916). The white dot marks where micro-sampling was performed.

Elemental analysis from Columbano's samples detected Pb and Cr in all samples, Ca on Columbano's T17 sample and Ba on Columbano's T26 sample. Raman analysis of Columbano's T17 sample identified monoclinic lead chromate characteristic bands at 325, 337, 357, 375, 399 cm^{-1} and 839 cm^{-1}. Calcium carbonate was also detected due to the presence of its characteristic CO_3^{2-} symmetric stretching at 1085 cm^{-1}. Columbano's T26 sample presents a slightly different spectrum, where the same CrO_4^{2-} bending bands show intensity shifts and a band at 970 cm^{-1} also appears, assigned to the SO_4^{2-} symmetric stretching. As stated above, this is due to the presence of mixed-crystals of lead chromate and lead sulphate. Representative spectra may be observed in figures 7A and 15B.

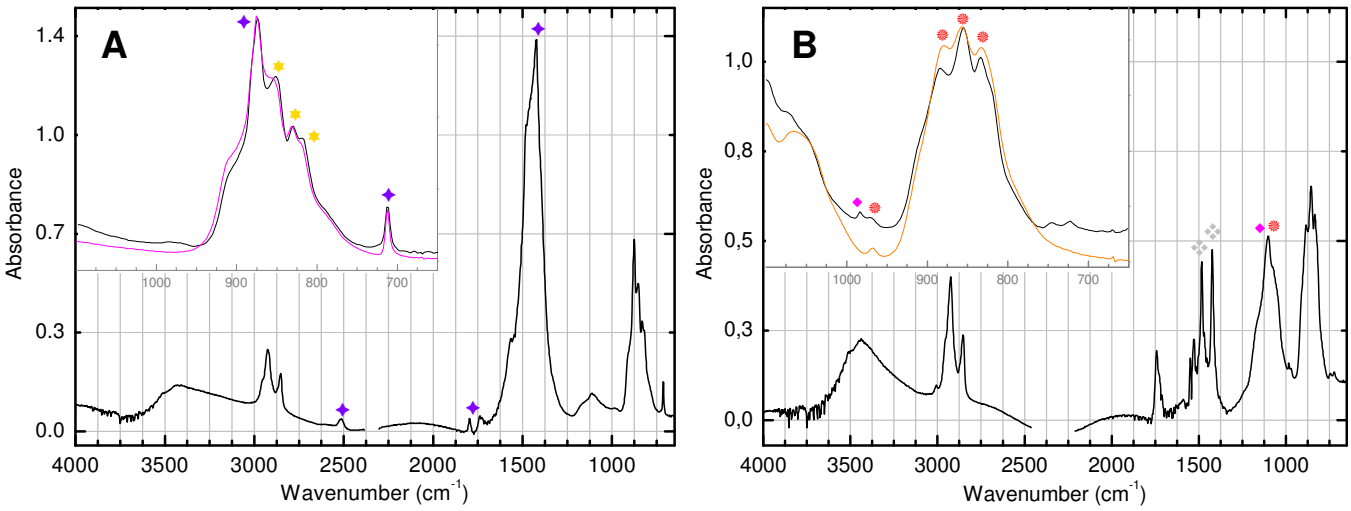


Figure 21. FTIR spectra of Columbano's oil paint tubes **A)** T17. Inset: T17 (black line) and [BMC.735].3 pigment (pink line), between 1100 and 650 cm^{-1}, and **B)** T26. Inset: T26 (black line) and [SLC.1163].3 pigment (orange line), between 1100 and 650 cm^{-1}. ✸ $PbCrO_4$; ✦ $CaCO_3$; ❁ $Pb(Cr,S)O_4$; ♦ $BaSO_4$; ❖ $MgCO_3$.

FTIR spectrum of Columbano's T17 sample (figure 21A) shows an intense and broad band at 1422 cm^{-1}, assigned to the CO_3^{2-} asymmetric stretching, characteristic of calcium carbonate, together with the bands at 875 cm^{-1} and 712, assigned to CO_3^{2-} asymmetric bending. Moreover, there is an overlap between the CrO_4^{2-} asymmetric stretching band at 853 cm^{-1} (shoulders at 831 and 820 cm^{-1}), characteristic of pure lead chromate, and the CO_3^{2-} asymmetric bending band at 875 cm^{-1}. A match between this sample and [BMC.735].3 pigment is presented. The latter is a pigment obtained from *Best Middle Chrome* [735] recipe, by adding a solution of lead nitrate to a solution of potassium dichromate and calcium carbonate, in the absence of sodium carbonate. Hence, it can be suggested that the chrome yellow pigment used in Columbano's T17 oil paint formulation was manufactured in a similar way as *Best Middle Chrome* [735] recipe but with a higher content of calcium carbonate (extender) and different proportions between potassium dichromate, lead nitrate and sodium carbonate; sufficient to prevent the formation of lead carbonate, which alters the CrO_4^{2-} asymmetric stretching profile. Lead carbonate is a secondary product formed in the complete recipe for *Best Middle Chrome* [735].

FTIR spectrum of Columbano's T26 sample (figure 21B) presents a CrO_4^{2-} asymmetric stretching profile (883, 854 and 833 cm^{-1}) characteristic of a high content of mixed-crystals of lead chromate and lead sulphate, as detected by μ-Raman. However, at 1101 cm^{-1} there is an overlap of the SO_4^{2-} asymmetric stretching bands of lead sulphate (shifted) and barium sulphate (extender). The presence of the latter is evident by its SO_4^{2-} symmetric stretching band at 984 cm^{-1}. A match between this sample and [SLC.1163].3 pigment was found. The latter pigment was obtained from *Super Lemon Chrome* [1163] recipe, where lead nitrate solution was added to a solution of potassium dichromate and sodium sulphate, in the absence of sodium carbonate. The only additive identified by μ-FTIR was magnesium carbonate with characteristic bands at 1483 and 1422 cm^{-1} (CO_3^{2-} asymmetric stretching). This compound was never found in any W & N chrome yellow recipe, which suggests that it was used as an additive in the oil paint formulation. It is suggested that the chrome yellow pigment used in Columbano's T26 oil paint formulation was manufactured by adding lead nitrate solution to a solution of potassium dichromate, sodium carbonate and some source of sulphate ions (in high amounts), such as sodium sulphate of sulphuric acid, without extenders.

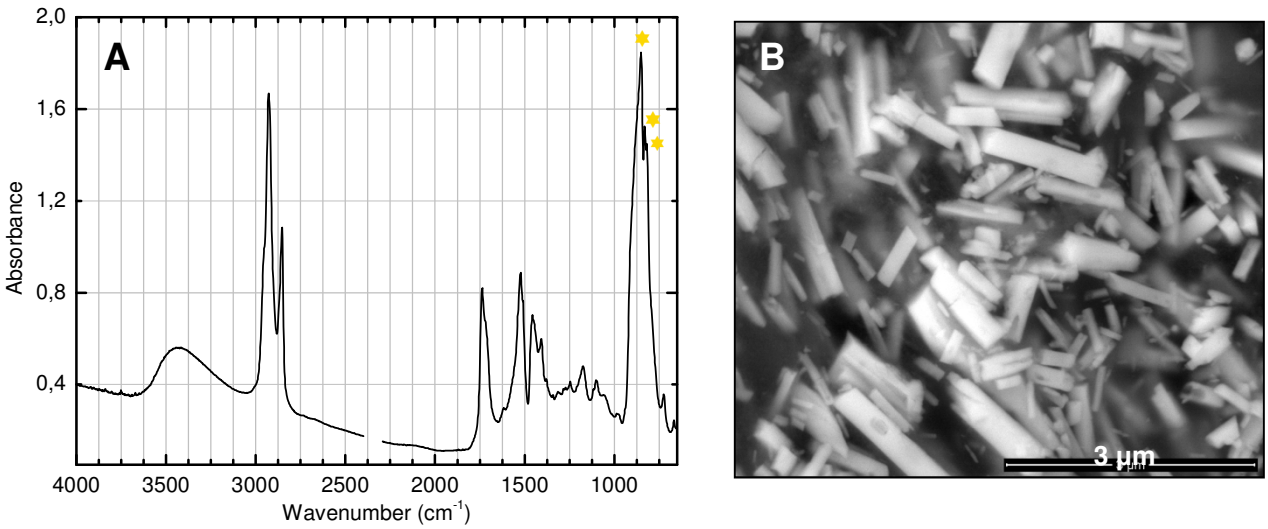


Figure 22. A) FTIR spectrum of Amadeo's oil paint tube ASC17 (*Jaune de Chrome foncé – Lefranc*) ✸ $PbCrO_4$, and **B)** SEM image in BSE mode of Amadeo's oil paint tube ASC17.

Elemental analysis of Amadeo's oil paint tubes detected only Pb and Cr. Raman analysis also identified monoclinic lead chromate characteristic bands at 325, 337, 357, 375, 399 cm^{-1} and 839 cm^{-1}. In Amadeo's ASC2 sample, lead carbonate was also detected due to the presence of its characteristic CO_3^{2-} symmetric stretching at 1054 cm^{-1}.

FTIR spectrum of Amadeo's ASC17 sample (figure 22A) does not show the presence of any extender, displaying a well defined CrO_4^{2-} asymmetric stretching profile, triply degenerate, with an intense band at 851 cm^{-1} (shoulders at 830 and 818 cm^{-1}), characteristic of pure lead chromate. This suggests that the chrome yellow pigment used in this oil paint formulation was produced without the addition of any ingredients beside the chrome and lead solutions. This is supported by SEM analysis (figure 22B) that identified only lead chromate rod-like particles, however, with several dimensions. No suggestion is given concerning the kind of chrome or lead solutions employed since Lefranc's colourman may have been using different compounds than W & N.

In the FTIR spectrum of Amadeo's ASC2 sample (figure 23A), it is possible to identify a high content of lead carbonate, with characteristic bands at 1400, 1051 cm^{-1} (CO_3^{2-} asymmetric stretching) and 678 cm^{-1} (CO_3^{2-} asymmetric bending). Lead carbonate was always a secondary product of the pigment syntheses performed, which is related to the use of sodium carbonate. As in the FTIR spectra of the synthesized pigments where this compound was formed, the CrO_4^{2-} asymmetric stretching profile is poorly defined at 855 and 839 cm^{-1}. No other compounds were detected in the ASC2 sample. A match between this sample and [SLC.1163].2 pigment was found. However, the CrO_4^{2-} asymmetric stretching profile is not as shifted to higher wavenumbers as it is in [SLC.1163].2. This is probably due to the presence of a small amount of mixed-crystals of lead chromate and lead sulphate, detected uniquely by FTIR given its SO_4^{2-} asymmetric and symmetric stretching bands at 1101, 1068 and 968 cm^{-1}. [SLC.1163].2 pigment is a pigment obtained from *Super Lemon Chrome* [1163] recipe, where lead nitrate solution was added to a solution of potassium dichromate and sodium carbonate in high amounts. Taking this into consideration, it is suggested that the chrome yellow pigment used in ASC2 oil paint formulation was produced by adding lead nitrate solution to a solution composed of a source of chromate ions, sodium carbonate and also some source of sulphate ions (in lower amounts).

A yellow micro-sample taken from Amadeo's paint box (CAM-JAP) has mixed-crystals of lead chromate and lead sulphate and barium sulphate as main components, as detected by FTIR (figure 23B). The CrO_4^{2-} asymmetric stretching profile (881, 855 and 833 cm^{-1}) is shifted from pure lead chromate to higher wavenumbers and an overlap between the SO_4^{2-} asymmetric stretching bands of lead sulphate and barium sulphate (extender) is also observed at 1170, 1101, 1067 cm^{-1}. Nevertheless, the presence of both is clear by their SO_4^{2-} symmetric stretching bands at 968 and 984 cm^{-1}, respectively. *Best Middle Chrome* [636] recipe has barium sulphate as extender and sulphuric acid is added. The yellow pigment from Amadeo's paint box could be formulated in a similar way to the above mentioned recipe but with higher amounts of barium sulphate and sulphuric acid.

Mixed-crystals of lead chromate and lead sulphate were also identified in the *Mucha* micro-samples (figure 24), together with viridian (characteristic bands at 3630-2630, 1288 and 1064 cm^{-1}). In the dark green sample, the CrO_4^{2-} asymmetric stretching profile is broader than usual, which may be due to the presence of viridian. In the light green sample this was not observed. No other compounds were detected. Probably, it is the same chrome yellow pigment mixed with different quantities of viridian. This pigment could be produced by adding a lead solution to a solution more rich in sulphate ions than chromate ions.

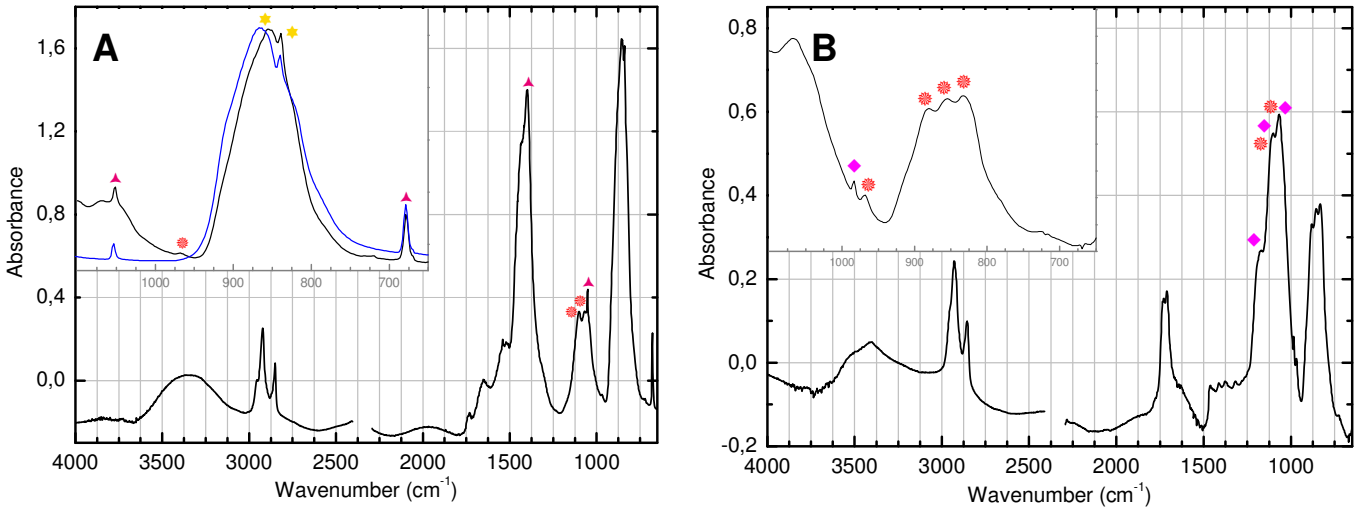


Figure 23. FTIR spectra of **A)** Amadeo's oil paint tube ASC2 (*Jaune de Chrome – tempera farge*). Inset: ASC2 (black line) and [SLC.1163].2 pigment (blue line) between 1100 and 650 cm^{-1}, and **B)** yellow micro-sample taken from Amadeo's paint box. Inset: between 1100 and 650 cm^{-1}. ★ $PbCrO_4$, ✺ $Pb(Cr,S)O_4$, ⅄ $PbCO_3$, ♦ $BaSO_4$.

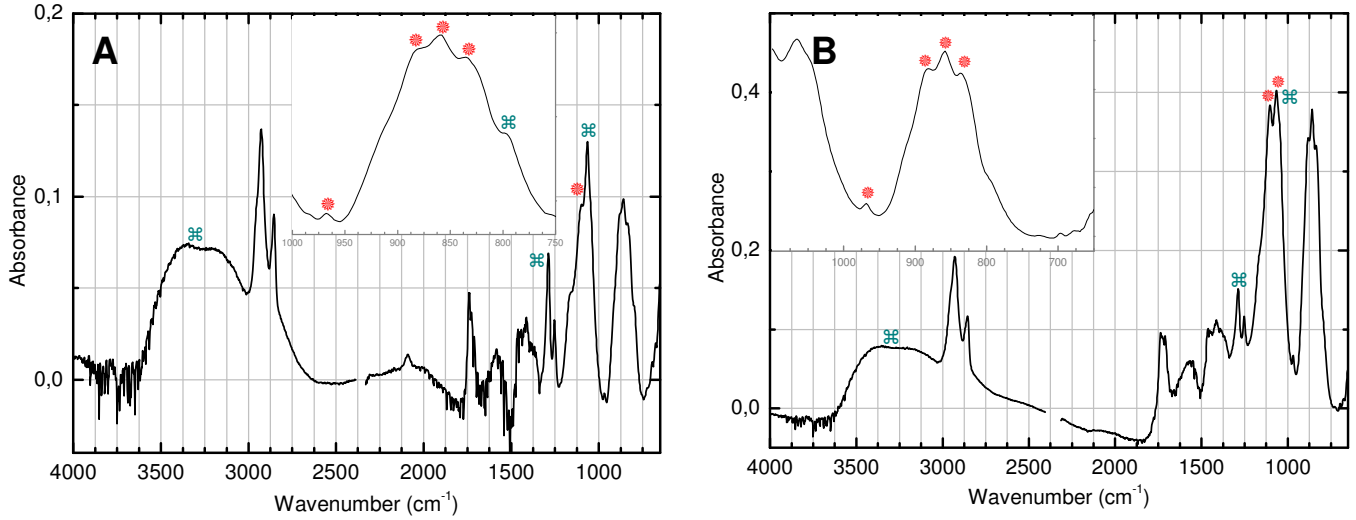


Figure 24. FTIR spectra of *Mucha* micro-samples **A)** dark green colour. Inset: between 1000 and 750 cm^{-1} and **B)** light green colour. Inset: between 1100 and 650 cm^{-1}. ✺ $Pb(Cr,S)O_4$, ⌘ $Cr_2O_3.2H_2O$ (viridian).

4. Conclusions

The manufacture of historically accurate chrome yellow pigments allowed a unique insight into Winsor & Newton's practices, choices and approach relating to this pigment. This work was the first to explore the value of the W & N database in relation to pigment manufacture. Although chemical terminology is antiquated or appears in acronyms (and is occasionally illegible or unclear) a correspondence between original materials and their current equivalent is suggested and may be consulted in Appendix II (Scale Down from Industrial to Laboratory Scale). Determination of sodium carbonate as the appropriate "soda" ingredient for chrome yellow manufacture was achieved experimentally.

Moreover, it was established that the rate of addition for ingredients is a fundamental parameter, which influences the pH and consequently the final pigment composition. It is suggested that W & N was manufacturing chrome yellow by adding each ingredient all at once, one after another.

Although the concept of pH was not available in the 19th century, the acid, neutral and basic concepts were already known and were definitely taken into consideration during chrome yellow manufacture. This was verified by all the reconstructions carried out, but most importantly by the *Best Yellow Chrome* [1227] recipe, where it is stated that lead solution is added until it neutralizes chrome solution. Moreover, sulphuric acid (acidic pH) was only used when lead subacetate (alkaline pH) was used as the lead solution.

The majority of yellow pigments obtained under neutral conditions are mainly composed of pure lead chromate ($PbCrO_4$). Under acidic conditions, lead chromate is also formed but when sulphate ions are introduced either by the addition of sodium sulphate or sulphuric acid, mixed crystals of lead chromate and lead sulphate ($Pb(Cr,S)O_4$) are formed. These compounds give rise to a lemon hue. On the other hand, pigments obtained under alkaline conditions have phoenicochroite (Pb_2CrO_5; basic lead chromate) as the main component. These pigments present an orange (sometimes reddish) colour. Also under alkaline conditions, other compounds were formed such as $K_2Pb_2(CrO_4)_3$ and $NaPb_2(CO_3)_2OH$. Their detection was possible only by XRD. XRD analysis allowed the identification of the majority of the pigments components. A semi-quantitative analysis was also possible. Furthermore, this analysis was facilitated by the previous µ-EDXRF analysis.

Raman analysis provided the identification of all the coloured compounds and extenders present in the pigments. Lead chromate, phoenicochroite and mixed-crystals of lead chromate and lead sulphate show very distinct spectra. However, in mixtures, only the main component of the pigments was detected by µ-Raman. Additionally, an unidentified Raman spectrum was obtained. Considering its bands it is suggested that it might correspond to $K_2Pb_2(CrO_4)_3$. The distinction between lead chromate and phoenicochroite was also possible by FTIR analysis, which also allowed their identification when both compounds were present. The CrO_4^{2-} asymmetric stretching profile of pure lead chromate has a very well defined structure, triply degenerate. When phoenicochroite is present, the latter structure is lost and the profile becomes sharper. The identification of mixed crystals of lead chromate and lead sulphate is straightforward. Furthermore, FTIR also allowed a semi-quantitative analysis between the coloured compounds and the extenders used. On the other hand, SEM analysis provided a morphological characterisation of the pigments from the complete recipes and the extenders used. It is possible to infer that different processes result in different particle shapes and sizes.

Additionally, lead carbonate and calcium carbonate were detected even though they were not added during the pigment manufacture. Lead carbonate was formed due to the similarity between its K_{sp} and that of lead chromate. Calcium carbonate was formed during [SLC.1163].5 manufacture. Calcium ions were introduced by the addition of calcium sulphate dihydrate, which reacted with the carbonate ions introduced by sodium carbonate. This seldom happens if sulphuric acid is added.

The characterisation of historically accurate chrome yellow pigments was carried out and a comparison between the synthesized pigments and samples from case studies was conducted. Lead chromate and mixed-crystals of lead chromate and lead sulphate were the only lead chromate based compounds detected in the case studies. The identified extenders were calcite, barytes and cerussite. Formulations for the chrome yellow pigments present in the case studies samples are proposed, taking into consideration W & N chrome yellow pigment formulations. This enhances artists' materials knowledge. This was only possible by means of a multi-analytical approach. Furthermore, it was proven that the W & N database provides easy and rapid access to a documentary source giving reliable information on 19th century artists' materials and their commercial preparation.

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